CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structure of 8-(4-methylphenyl)-2′-deoxyadenosine hemihydrate

Ajaykumar V. Ardhapure,[a] Yogesh S. Sanghvi,[b] Yulia Borozdina,[c] Anant Ramakant Kapdi[a] and Carola Schulzke[d]*

[a]Department of Chemistry, Institute of Chemical Technology, Nathalal Parekh Road, Matunga, Mumbai 400 019, India, [b]Rasayan Inc. 2802, Crystal Ridge Road, Encinitas, California 92024-6615, USA, [c]Max Planck Institute for Biological Cybernetics Spemannstrasse 41, D-72076 Tübingen, Germany, and [d]Institut für Biochemie, Ernst-Moritz-Arndt Universität Greifswald, Felix-Hausdorff-Strasse 4, D-17487 Greifswald, Germany. *Correspondence e-mail: carola.schulzke@uni-greifswald.de

Received 24 September 2017
Accepted 30 November 2017

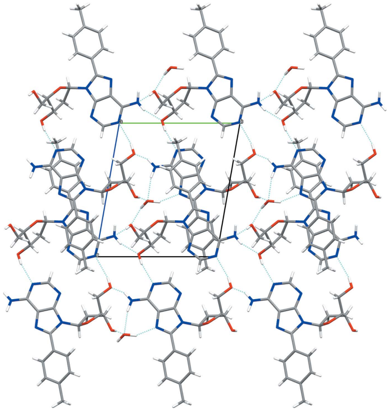
Edited by P. Bombicz, Hungarian Academy of Sciences, Hungary

Keywords: crystal structure; adenosine; nucleoside; palladium; catalysis; Suzuki–Miyaura cross-coupling.

CCDC reference: 1588387

Supporting information: this article has supporting information at journals.iucr.org/e

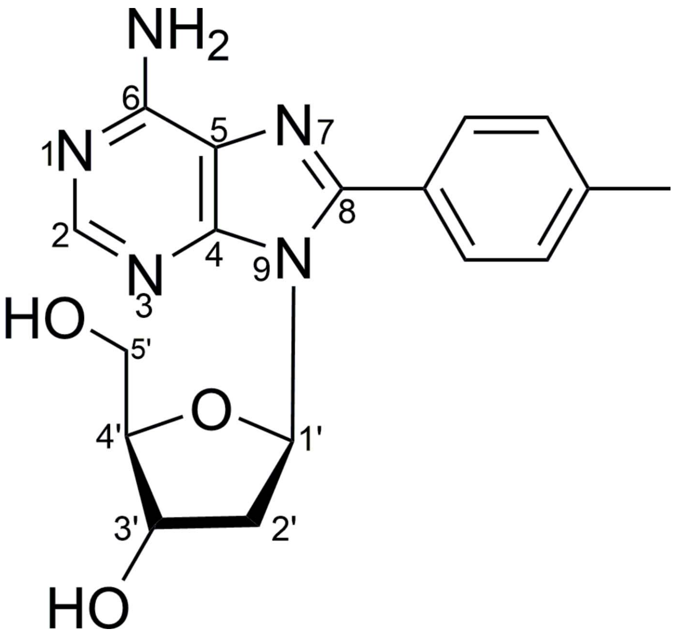
In the asymmetric unit, equalling the unit cell (triclinic, $P1$, $Z = 1$), two molecules of the title compound, 8-(4-methylphenyl)-D-2′-deoxyadenosine, $C_{17}H_{19}N_5O_3$, are present, with distinct conformations of the two sugar moieties, together with one solvent water molecule. All three ribose O atoms are involved in hydrogen bonding and the crystal packing is largely determined by hydrogen-bonding or hydrogen–heteroatom interactions (O—H⋯O, O—H⋯N, N—H⋯O, C—H⋯O and C—H⋯N) with one independent molecule directly linked to four neighbouring molecules and the other molecule directly linked to six neighbouring molecules. The two independent molecules of the asymmetric unit display three weak intramolecular C—H-to-heteroatom contacts, two of which are very similar despite the different conformations of the deoxyribosyl moieties. The aromatic ring systems of both molecules are in proximity to each other and somehow aligned, though not coplanar. The absolute structures of the two molecules were assumed with reference to the reactant 8-bromo-D-2′-deoxyadenosine as they could not be determined crystallographically.



1. Chemical context

Alkyl, alkenyl or alkynyl modified purines are known for having interesting biological activities. Many of these modified nucleosides show, for instance, potential for/activity as drug candidates, biological probes *etc* (Manfredini *et al.*, 1995). Attempts to implement green, *i.e.* eco-friendly, procedures for the synthesis of modified nucleosides involve the use of palladium complexes as active catalysts because of their proven ability to perform such catalytic transformations even in aqueous media (Agrofoglio *et al.*, 2003; Gayakhe *et al.*, 2016). Modifying the nucleoside bases by substitution of the C—H functions of purine and pyrimidine can be utilized for instance to install or increase fluorescence properties. Fluorescent nucleosides might then be employed as probes for studying the impact of changes in the biological environment: DNA damage, drug–DNA or protein–DNA interactions for instance. Such DNA probes are relevant for both chemical biologists as well as bio-organic chemists (Tanpure *et al.*, 2013). Structural elucidation of substituted nucleosides in general will aid our understanding of mechanistic aspects in this respect and provide a basis for *in silico* studies. The synthesis and crystal structure of the title compound, 8-(4-methylphenyl)-D-2′-deoxyadenosine are presented here as part of our studies in this regard.

https://doi.org/10.1107/S2056989017017212



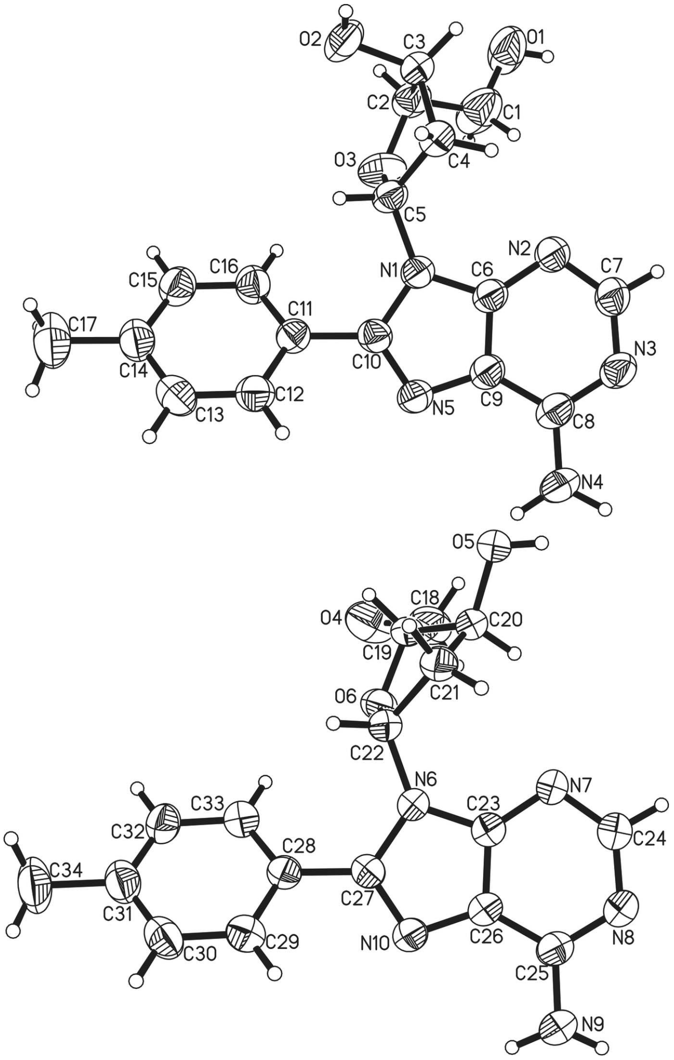


Figure 1
The two independent compound molecules of the asymmetric unit displayed in a comparable orientation to show the distinct conformation of the deoxyribosyl moiety (top: mole 1; bottom: mole 2). Displacement ellipsoids are shown at the 50% probability level.

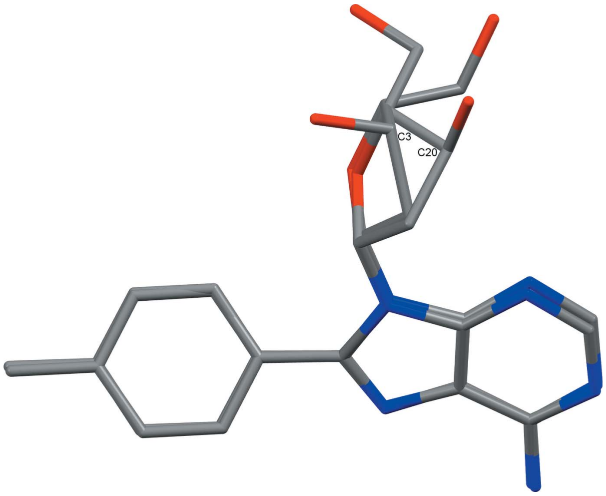


Figure 2
The two crystallographically independent molecules of the asymmetric unit overlaid. The root-mean-square deviation (rmsd) and the maximum distance between atom positions are 0.8296 and 2.6760 Å, respectively.

2. Structural commentary

In the title compound, two molecules of $C_{17}H_{19}N_5O_3$ crystallize together with one molecule of water in the triclinic space group $P1$ with $Z = 1$. The two molecules (mole 1 and mole 2, Figs. 1 and 2) differ in the puckering of the deoxyribose sugar, which is the most interesting feature of this novel molecular structure. In mole 1 with 3′-exo puckering, the –CH$_2$—OH substituent on C2 (in the $C^{4'}$ position according to typical nucleoside labelling, see Scheme) and the hydroxyl substituent on C3 ($C^{3'}$ position) are both axial or rather axial, whereas in mole 2 with 3′-endo puckering they are both equatorial. For the parent molecule, D-deoxyadenosine, two crystal structures are available in the literature: one in pure form (Sato, 1984) and one as the monohydrate (Storr *et al.*, 2009). In the absence of water, the sugar adopts the 3′-endo confirmation with $C^{3'}$ above the $C^{4'}$–O–$C^{1'}$ plane by 0.5 Å (Sato, 1984). In the presence of water, both the oxygen and hydrogen atoms of the hydroxyl substituent on C3′ are involved in hydrogen bonds with water and the sugar adopts the 3′-exo ring pucker with $C^{3'}$ below the $C^{4'}$–O–$C^{1'}$ plane by 0.52 Å (Storr *et al.*, 2009). Hydrogen bonding in the crystal lattice apparently influences the ring pucker of deoxyribose moieties. In the present structure, bearing two molecules with distinct ring pucker, the hydroxyl group bound to C3′ of the 3′-exo form (mole 1) is involved in one hydrogen bond as donor with water (O2—H2*O*···O7$^{\mathrm{ii}}$; see Table 1 for distances and angles) and that of the 3′-endo form (mole 2) is involved in bifurcated hydrogen bonding with two purine moieties (O5—H5*O*···N3$^{\mathrm{vi}}$ and N9—H9*N*···O5$^{\mathrm{ii}}$). Here $C^{3'}$ is located 0.45 Å below (mole 1) and 0.82 Å above (mole 2) the respective $C^{4'}$–O–$C^{1'}$ planes. The methylene–hydroxyl oxygen atom O4 on C19 (exo-$C^{4'}$; mole 2) is involved as acceptor in a hydrogen bond with the water molecule (O7—H70*O*···O4$^{\mathrm{vii}}$).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···N8$^{\rm i}$	0.82	2.14	2.943 (5)	168
O2—H2*O*···O7$^{\rm ii}$	0.82	1.93	2.743 (5)	172
C1—H1*A*···N2	0.97	2.69	3.557 (7)	149
C4—H4*A*···N2	0.97	2.37	3.099 (5)	131
C16—H16···O3	0.93	2.49	3.257 (5)	140
C7—H7···N7$^{\rm i}$	0.93	2.66	3.374 (6)	135
N4—H40*N*···O1$^{\rm iii}$	0.91 (3)	2.27 (4)	3.033 (6)	142 (4)
N4—H4*N*···O7$^{\rm iv}$	0.92 (3)	2.05 (3)	2.955 (6)	166 (5)
O4—H4*O*···N9$^{\rm v}$	0.82	2.22	3.039 (5)	175
O5—H5*O*···N3$^{\rm vi}$	0.82	2.00	2.805 (4)	166
C20—H20···N7	0.98	2.56	3.201 (5)	123
C21—H21*B*···N7	0.97	2.47	2.992 (5)	113
C32—H32···O1$^{\rm iii}$	0.93	2.65	3.572 (6)	171
C33—H33···O6	0.93	2.50	3.288 (5)	143
N9—H9*N*···O5$^{\rm ii}$	0.92 (3)	2.01 (3)	2.903 (5)	164 (4)
O7—H7*O*···N5$^{\rm vii}$	0.98 (5)	1.87 (6)	2.789 (4)	154 (6)
O7—H70*O*···O4$^{\rm vii}$	0.99 (5)	1.82 (6)	2.761 (5)	159 (7)
O4—H4*O*···N9	0.82	2.22	3.039 (5)	175

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

The aromatic six-membered rings of the two distinct molecules are to some extent aligned with each other, forming pairs of phenyl and pyrimidine rings. They are neither coplanar nor perfectly overlaid, however. The respective planes for the mole 1 phenyl ring and mole 2 pyrimidine ring pair are at an angle of 15.1 (2)° and those of the mole 1 pyrimidine ring and mole 2 phenyl ring pair exhibit an angle of 14.6 (2)°. The centroid–centroid distance for the former pair is 3.652 (3) Å and it is 3.621 (3) Å for the latter. The intramolecular angles between the planes of the aromatic six-membered ring systems are 36.8 (2) and 36.5 (2)° for mole 1 and mole 2, respectively, *i.e.* very similar.

In both molecules, the conformation of the base with respect to the ribose moiety is *syn*, *i.e.* the pyrimidine ring and the deoxyribose moiety face the same direction. This is in contrast to the two known structures of D-deoxyadenosine (Sato, 1984; Storr *et al.*, 2009) and one structure of a derivative with an inverted configuration at $C^{3'}$ (Robins *et al.*, 2007) but in accordance with the six other derivatives bearing a substituent at the C^{8} position (here C10 and C27) and no further substituents on deoxyadenosine that are reported in the literature (Vrábel *et al.*, 2007; Storr *et al.*, 2009, 2010). In all six cases, the substituents are aromatic in nature and more sterically demanding than the pyrimide ring of the purine base. The glycosidic torsion angles $O—C^{1'}—N^{9}—C^{4}$ for the unsubstituted structures range from −94.76° (Robins *et al.*, 2007) to the more usual −178.74° (Storr *et al.*, 2009) for unsubstituted deoxyadenosine structures with an *anti* conformation. For substituted structures, which are in a *syn* conformation, these angles range from 48.73° for a *p*-fluoro-*p*-biphenyl substituent to 91.90° for a *p*-methoxyphenyl substituent (Storr *et al.*, 2009). Here the respective torsion angles are 87.40° for mole 1 and 86.32° for mole 2, suggesting that this torsion angle and the pucker mode are independent of each other.

Bond lengths and angles of the purine bases in the two molecules are very similar to previously reported values in related compounds. As is typical, the bond between C^{5} and C^{6} is the longest [mole 1, C8—C9, 1.409 (6) Å; mole 2, C25—C26, 1.393 (5) Å] and the bond between N^{7} and C^{8} is the shortest [mole 1, N5—C10, 1.315 (5) Å; mole 2, N10—C27, 1.323 (5) Å] of the planar heterocyclic ring system. For mole 2, these values are close to the low and high ends, respectively, of the reported values whereas those of mole 1 are rather average. For the deoxyribose ring, the shortest distance is usually found for the $O—C^{1'}$ bond as is the case here. The locations of the longest bonds do vary. Most often it is the $C^{3'}—C^{4'}$ bond. However, in case of mole 1 it is $C^{2'}—C^{3'}$ [C3—C4, 1.532 (6) Å] and for mole 2 it is $C^{1'}—C^{2'}$ [C21—C22, 1.532 (5) Å], neither of which being unprecedented (Storr *et al.*, 2009, 2010). Most values found here fall inside the observed ranges for sugar moieties, the link between the sugar and base or the purine bases of the three known unsubstituted and the six substituted structures of D-2′-deoxyadenosine. The exceptions are $C^{3'}—C^{4'}$ for mole 1 [C2—C3, 1.504 (7) Å; range of literature known structures is 1.509–1.549 Å], $C^{4}—N^{3}$ for mole 2 [C23—N7, 1.332 (5) Å; range in the literature is 1.336–1.357 Å] and $C^{5}—N^{7}$ for both moles [C9—N5, 1.378 (5) Å, C26—N10, 1.377 (5) Å; range 1.380–1.394 Å], all of which being the shortest observed to date. No systematic influence of the substituent on the deoxyadenosine backbone with respect to distances and angles of the parent molecule was observed as closely related compounds (phenyl-, *p*-methoxyphenyl (both Storr *et al.*, 2009) and *p*-methylphenyl (this work) do not exhibit apparent similarities in this regard.

3. Supramolecular features

In the crystal, molecules are linked by O—H···O, O—H···N, N—H···O, C—H···O and C—H···N classical and non-classical hydrogen-bonding contacts (Fig. 3 and Table 1), forming a three-dimensional network.

The water O atom (O7) utilizes both hydrogen atoms and both lone pairs to act as a hydrogen-bonding donor and acceptor with two nitrogen atoms (N4—O7$^{\rm iv}$, O7—H7*O*···N5$^{\rm vii}$) of the purine base of mole 1, as donor to the hydroxymethyl oxygen atom (O7—H70*O*···O4$^{\rm vii}$) of mole 2 and as acceptor from the hydroxyl oxygen atom (O2-–H2*O*···O7$^{\rm ii}$) of mole 1. Mole 1 is directly linked to four neighbouring molecules [(1) N4—H40*N*···O1$^{\rm iii}$, (2) N3···H5*O*—O5$^{\rm i}$, C7—H7···N7$^{\rm i}$, and O1—H1*O*···N8$^{\rm i}$, (3) O1···H40*N*$^{\rm ii}$—N4, (4) C32—H32···O1$^{\rm ii}$] plus further four mediated by water. Mole 2 is in direct contact with six neighbouring molecules [(1) C32—H32···O1$^{\rm iii}$, (2) O4—H4*O*···N9$^{\rm v}$, (3) N9—H9*N*···O5$^{\rm ii}$, (4) O5—H5*O*···N3$^{\rm vi}$, N7···H7—C7$^{\rm vi}$, and N8···H1*O*—O1$^{\rm vi}$,(5) O5···H9—N9$^{\rm iii}$, (6) N9···H4*O*—O4$^{\rm viii}$) plus further two mediated by water.

4. Synthesis and crystallization

The title compound, 8-(4-methylphenyl)-D-2′-deoxyadenosine was synthesized based on a recently reported method (Bhilare *et al.*, 2016). The compound was obtained by the cross-coupling reaction of 8-bromo-2′-deoxyadenosine and

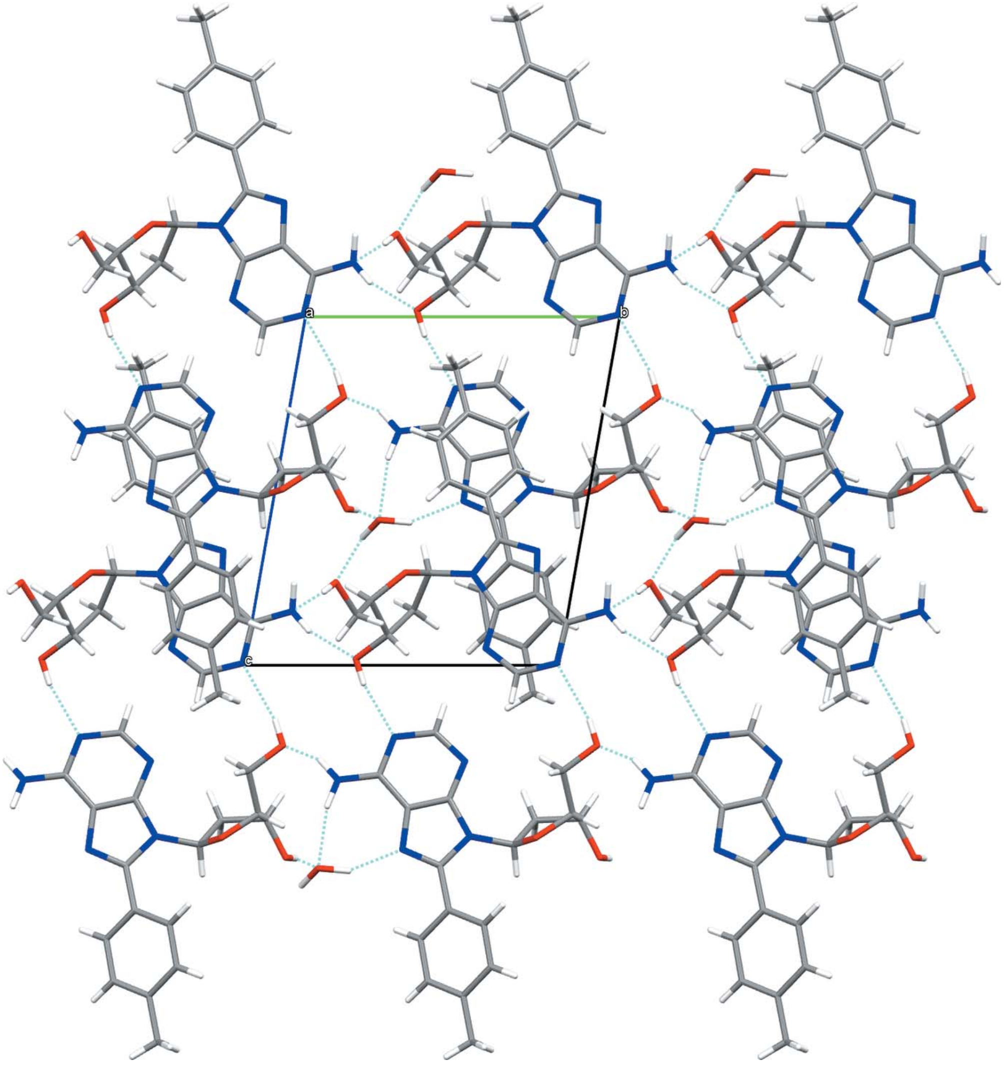


Figure 3
The crystal packing (*Mercury 3.19*; Macrae *et al.*, 2006) viewed along the *a* axis, showing the classical hydrogen bonds forming a three-dimensional network.

4-methylphenyl boronic acid in the presence of Pd(OAc)$_2$ and PTABS (phospha-tris-aza-adamantyl-butane-saltone) ligand in neat water. The reaction was carried out in a Schlenk tube using a Schlenk system under a nitrogen atmosphere. All other reagents and solvents were purchased commercially and used without any further purification.

Synthesis of 8-(4-methylphenyl)-D-2′-deoxyadenosine: To a solution of palladium acetate (1.12 mg, 1.0 mol %) and PTABS ligand (2.93 mg, 2.0 mol %) in degassed water (1.0 ml) at ambient temperature under N$_2$ was added 8-bromo-D-2′-deoxyadenosine (0.5 mmol) and the solution was stirred for 5 min at 353 K. The reaction mixture was allowed to cool to room temperature and then 4-(methyl)phenyl boronic acid (0.75 mmol) was added along with triethylamine (0.14 ml, 1 mmol) and degassed water (2.0 ml). The resulting solution was then stirred at 353 K for 12 h. The reaction progress was observed by TLC analysis. After the completion of the reaction, the solvent was removed *in vacuo* and the resultant residue obtained was purified using column chromatography in a CH$_2$Cl$_2$:MeOH solvent system (96:4) to afford the desired product as a white solid (143 mg, 84% yield). UV–visible absorption and fluorescence emission in methanol (10 µM) λ_{abs} = 301 nm, λ_{fl} = 371 nm. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.15 (*s*, 1H), 7.66 (*d*, *J* = 8.1 Hz, 2H), 7.47 (*d*, *J* = 8.2 Hz, 4H), 6.15 (*t*, *J* = 7.3 Hz, 1H), 5.56 (*s*, 1H), 5.30 (*d*, *J* = 18.0 Hz, 1H), 4.47 (*s*, 1H), 3.88 (*s*, 1H), 3.74–3.49 (*m*, 2H), 3.30 (*m*, 1H), 2.56 (*s*, 3H), 2.14 (*dd*, *J* = 12.2, 5.7 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.9, 151.7, 150.1, 149.7, 141.1, 129.6, 125.4, 125.2, 119.0, 88.1, 85.4, 71.2, 62.0, 45.0, 36.8. ESI–MS (*m*/*z*) = 374 (M^+ + H$^+$). Analysis calculated for C$_{17}$H$_{19}$N$_5$O$_3$: C, 59.81; H, 5.61; N, 20.52. Found: C, 59.68; H, 5.46; N, 20.44.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

The hydrogen atoms of water and the two –NH$_2$ groups were located but refined with constraints (*SHELXL* instruction: SADI 0.05 O7 H7*O* O7 H70*O* and SADI 0.05 N4 H4*N* N4 H40*N* N9 H9*N* N9 H90*N*). The hydrogen atoms of the hydroxyl groups were attached with a riding model [*SHELXL* instruction: HFIX 147; $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm O})$] with the orientation taken from the actually present electron density. When refined freely, the O—H distances became very long while using distance constraints did not improve the refinement compared with HFIX. The C-bound hydrogen atoms were included in calculated positions and treated as riding: C—H = 0.93–0.98 Å with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$ for methyl groups and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ for all other C—H bonds.

Acknowledgements

ARK and CS acknowledge 'The Alexander von Humboldt Foundation' for the research cooperation programme which is also thanked for the equipment grant to ARK. YB and CS gratefully acknowledge funding from the ERC.

Funding information

Funding for this research was provided by: Alexander von Humboldt-Stiftung (grant No. 3.4-IP-DEU/1131213 to Anant R. Kapdi, Carola Schulzke); FP7 Ideas: European Research Council (grant No. 281257 to Carola Schulzke).

References

Agrofoglio, L. A., Gillaizeau, I. & Saito, Y. (2003). *Chem. Rev.* **103**, 1875–1916.
Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Bhilare, S., Gayakhe, V., Ardhapure, A. V., Sanghvi, Y. S., Schulzke, C., Borozdina, Y. & Kapdi, A. R. (2016). *RSC Adv.* **6**, 83820–83830.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Gayakhe, V., Ardhapure, A., Kapdi, A. R., Sanghvi, Y. S., Serrano, J. L., García, L., Pérez, J., García, J., Sánchez, G., Fischer, C. & Schulzke, C. (2016). *J. Org. Chem.* **81**, 2713–2729.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Manfredini, S., Baraldi, P. G., Bazzanini, R., Marangoni, M., Simoni, D., Balzarini, J. & De Clercq, E. (1995). *J. Med. Chem.* **38**, 199–203.
Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.
Robins, M. J., Nowak, I., Wnuk, S. F., Hansske, F. & Madej, D. (2007). *J. Org. Chem.* **72**, 8216–8221.
Sato, T. (1984). *Acta Cryst.* C**40**, 880–882.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Stoe & Cie (2010). *X-AREA*. Stoe & Cie, Darmstadt, Germany.
Storr, T. E., Baumann, C. G., Thatcher, R. J., De Ornellas, S., Whitwood, A. C. & Fairlamb, I. J. S. (2009). *J. Org. Chem.* **74**, 5810–5821.
Storr, T. E., Strohmeier, J. A., Baumann, C. G. & Fairlamb, I. J. S. (2010). *Chem. Commun.* **46**, 6470–6472.
Tanpure, A. A., Pawar, M. G. & Srivatsan, S. G. (2013). *Isr. J. Chem.* **53**, 366–378.
Vrábel, M., Pohl, R., Klepetářová, B., Votruba, I. & Hocek, M. (2007). *Org. Biomol. Chem.* **5**, 2849–2857.

Table 2
Experimental details.

Crystal data	
Chemical formula	$2{\rm C}_{17}{\rm H}_{19}{\rm N}_5{\rm O}_3\cdot{\rm H}_2{\rm O}$
$M_{\rm r}$	700.76
Crystal system, space group	Triclinic, *P*1
Temperature (K)	293
a, *b*, *c* (Å)	7.3991 (15), 10.637 (2), 11.931 (2)
α, β, γ (°)	93.65 (3), 107.37 (3), 108.11 (3)
V (Å^3)	839.1 (3)
Z	1
Radiation type	Mo *K*α
μ (mm^{-1})	0.10
Crystal size (mm)	0.29 × 0.17 × 0.12
Data collection	
Diffractometer	Stoe IPDS2T
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7187, 5713, 4036
$R_{\rm int}$	0.033
$(\sin \theta/\lambda)_{\rm max}$ (Å^{-1})	0.638
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.041, 0.110, 1.00
No. of reflections	5713
No. of parameters	490
No. of restraints	10
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max}$, $\Delta\rho_{\rm min}$ (e Å^{-3})	0.29, −0.20
Absolute structure	Flack *x* determined using 1312 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons et al., 2013)

Computer programs: *X-AREA* (Stoe & Cie, 2010), *SIR92* (Altomare *et al.*, 1994), *SHELXL2016* (Sheldrick, 2015) and *WinGX* (Farrugia, 2012), *XP* in *SHELXTL* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2006) and *CIFTAB* (Sheldrick, 2015).

supporting information

Acta Cryst. (2018). E**74**, 1-5   [https://doi.org/10.1107/S2056989017017212]

Crystal structure of 8-(4-methylphenyl)-2′-deoxyadenosine hemihydrate

Ajaykumar V. Ardhapure, Yogesh S. Sanghvi, Yulia Borozdina, Anant Ramakant Kapdi and Carola Schulzke

Computing details

Data collection: *X-AREA* (Stoe & Cie, 2010); cell refinement: *X-AREA* (Stoe & Cie, 2010); data reduction: *X-AREA* (Stoe & Cie, 2010); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015) and *WinGX* (Farrugia, 2012); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *CIFTAB* (Sheldrick, 2015).

8-(4-Methylphenyl)-2′-deoxyadenosine hemihydrate

Crystal data

$2C_{17}H_{19}N_5O_3 \cdot H_2O$
$M_r = 700.76$
Triclinic, $P1$
$a = 7.3991\ (15)$ Å
$b = 10.637\ (2)$ Å
$c = 11.931\ (2)$ Å
$\alpha = 93.65\ (3)°$
$\beta = 107.37\ (3)°$
$\gamma = 108.11\ (3)°$
$V = 839.1\ (3)$ Å^3
$Z = 1$
$F(000) = 370$
$D_x = 1.387$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 7187 reflections
$\theta = 6.4–53.9°$
$\mu = 0.10$ mm^{-1}
$T = 293$ K
Rhomb, colourless
0.29 × 0.17 × 0.12 mm

Data collection

Stoe IPDS2T
  diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 6.67 pixels mm^{-1}
ω scans
7187 measured reflections
5713 independent reflections
4036 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.033$
$\theta_{\text{max}} = 27.0°$, $\theta_{\text{min}} = 3.2°$
$h = -9 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = -15 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.110$
$S = 1.00$
5713 reflections
490 parameters
10 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent
  and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.065P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} < 0.001$
$\Delta\rho_{\text{max}} = 0.28$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.20$ e Å^{-3}
Absolute structure: Flack x determined using
  1312 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons et al., 2013)

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.

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

	x	*y*	*z*	$U_{\rm iso}*/U_{\rm eq}$
O1	−0.0436 (7)	1.1671 (4)	0.2298 (3)	0.0884 (13)
H1O	−0.097552	1.129571	0.160023	0.133*
O2	0.4464 (5)	1.2386 (3)	0.5518 (3)	0.0652 (9)
H2O	0.563957	1.269834	0.554191	0.098*
O3	0.0583 (4)	1.0235 (3)	0.4948 (3)	0.0600 (8)
N1	0.0975 (5)	0.8132 (3)	0.4909 (3)	0.0420 (8)
N2	0.0200 (5)	0.7555 (3)	0.2751 (3)	0.0502 (9)
N3	−0.1330 (5)	0.5172 (3)	0.2056 (3)	0.0519 (9)
N4	−0.2060 (6)	0.3617 (4)	0.3286 (4)	0.0615 (11)
N5	−0.0280 (5)	0.6057 (3)	0.5288 (3)	0.0433 (8)
C1	−0.0454 (10)	1.0721 (5)	0.3029 (5)	0.0878 (19)
H1A	−0.018480	0.998584	0.266890	0.105*
H1B	−0.178735	1.036543	0.309416	0.105*
C2	0.1090 (7)	1.1277 (4)	0.4265 (4)	0.0565 (12)
H2	0.095003	1.209404	0.459880	0.068*
C3	0.3265 (7)	1.1525 (4)	0.4398 (4)	0.0525 (11)
H3	0.361711	1.190427	0.373226	0.063*
C4	0.3418 (6)	1.0125 (4)	0.4446 (4)	0.0466 (9)
H4A	0.293488	0.959503	0.365506	0.056*
H4B	0.478870	1.017134	0.485890	0.056*
C5	0.2028 (6)	0.9575 (3)	0.5149 (4)	0.0409 (8)
H5	0.284651	0.982718	0.599710	0.049*
C6	0.0214 (5)	0.7262 (4)	0.3837 (3)	0.0418 (9)
C7	−0.0600 (7)	0.6446 (4)	0.1936 (4)	0.0528 (11)
H7	−0.065826	0.658151	0.116535	0.063*
C8	−0.1309 (6)	0.4903 (4)	0.3151 (4)	0.0476 (10)
C9	−0.0530 (6)	0.6002 (4)	0.4092 (4)	0.0429 (9)
C10	0.0600 (5)	0.7341 (4)	0.5750 (3)	0.0399 (9)
C11	0.1178 (5)	0.7870 (4)	0.7025 (4)	0.0405 (9)
C12	0.1870 (6)	0.7128 (4)	0.7855 (4)	0.0475 (10)
H12	0.194438	0.630720	0.759860	0.057*
C13	0.2450 (6)	0.7593 (5)	0.9061 (4)	0.0547 (11)
H13	0.291305	0.707810	0.960356	0.066*
C14	0.2358 (6)	0.8806 (5)	0.9481 (4)	0.0547 (11)
C15	0.1588 (7)	0.9530 (5)	0.8648 (4)	0.0544 (11)
H15	0.147807	1.033659	0.890854	0.065*
C16	0.0983 (6)	0.9064 (4)	0.7434 (4)	0.0497 (10)
H16	0.044545	0.955128	0.688939	0.060*
C17	0.3074 (9)	0.9341 (7)	1.0797 (5)	0.0809 (16)

H17A	0.441281	0.999192	1.103230	0.121*
H17B	0.308729	0.861573	1.123501	0.121*
H17C	0.217986	0.975718	1.096240	0.121*
H40N	−0.216 (7)	0.295 (4)	0.273 (4)	0.068 (15)*
H4N	−0.200 (9)	0.342 (6)	0.404 (3)	0.085 (18)*
O4	0.0629 (5)	0.2449 (4)	0.7618 (3)	0.0816 (12)
H4O	−0.028481	0.212598	0.788312	0.122*
O5	0.6871 (5)	0.3508 (3)	0.9814 (3)	0.0555 (8)
H5O	0.744943	0.388280	1.051057	0.083*
O6	0.4002 (4)	0.4607 (2)	0.7339 (2)	0.0446 (6)
N6	0.6124 (5)	0.6764 (3)	0.7384 (3)	0.0388 (7)
N7	0.7163 (5)	0.7581 (3)	0.9512 (3)	0.0472 (8)
N8	0.7603 (5)	0.9933 (3)	0.9942 (3)	0.0491 (9)
N9	0.7062 (6)	1.1223 (3)	0.8448 (3)	0.0503 (9)
N10	0.5980 (5)	0.8685 (3)	0.6717 (3)	0.0409 (7)
C18	0.2362 (7)	0.3301 (5)	0.8554 (5)	0.0633 (13)
H18A	0.261470	0.284895	0.923486	0.076*
H18B	0.213785	0.411095	0.879997	0.076*
C19	0.4151 (6)	0.3660 (4)	0.8140 (3)	0.0432 (9)
H19	0.421093	0.285073	0.773577	0.052*
C20	0.6147 (6)	0.4399 (4)	0.9122 (3)	0.0410 (9)
H20	0.599021	0.508260	0.963841	0.049*
C21	0.7459 (6)	0.5074 (4)	0.8419 (3)	0.0435 (9)
H21A	0.808272	0.448407	0.816158	0.052*
H21B	0.850804	0.589849	0.889000	0.052*
C22	0.5983 (6)	0.5365 (3)	0.7348 (3)	0.0392 (8)
H22	0.616428	0.504592	0.661376	0.047*
C23	0.6656 (5)	0.7723 (4)	0.8371 (3)	0.0395 (9)
C24	0.7619 (7)	0.8731 (4)	1.0220 (4)	0.0544 (11)
H24	0.800784	0.869971	1.103164	0.065*
C25	0.7055 (5)	1.0019 (4)	0.8780 (4)	0.0415 (9)
C26	0.6558 (6)	0.8884 (4)	0.7942 (3)	0.0391 (8)
C27	0.5714 (5)	0.7408 (4)	0.6401 (3)	0.0384 (9)
C28	0.5122 (5)	0.6778 (4)	0.5165 (3)	0.0397 (9)
C29	0.5855 (6)	0.7548 (4)	0.4390 (4)	0.0466 (10)
H29	0.671644	0.843321	0.467040	0.056*
C30	0.5305 (7)	0.6997 (5)	0.3202 (4)	0.0537 (11)
H30	0.580047	0.752242	0.269235	0.064*
C31	0.4041 (7)	0.5690 (5)	0.2762 (4)	0.0534 (11)
C32	0.3301 (6)	0.4924 (4)	0.3528 (4)	0.0514 (10)
H32	0.244670	0.403800	0.324119	0.062*
C33	0.3815 (6)	0.5460 (4)	0.4717 (4)	0.0455 (9)
H33	0.328588	0.493749	0.521693	0.055*
C34	0.3460 (9)	0.5077 (6)	0.1468 (4)	0.0801 (16)
H34A	0.390460	0.432367	0.142542	0.120*
H34B	0.408834	0.573573	0.105929	0.120*
H34C	0.202055	0.478320	0.110063	0.120*
H9N	0.703 (7)	1.185 (4)	0.900 (3)	0.056 (13)*

H90N	0.621 (8)	1.113 (7)	0.768 (3)	0.10 (2)*
O7	0.8496 (5)	0.3480 (3)	0.5826 (3)	0.0684 (9)
H7O	0.909 (10)	0.446 (5)	0.590 (6)	0.11 (2)*
H70O	0.937 (11)	0.305 (7)	0.632 (7)	0.14 (3)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.142 (4)	0.065 (2)	0.051 (2)	0.051 (2)	0.006 (2)	0.0055 (17)
O2	0.067 (2)	0.0471 (17)	0.061 (2)	−0.0004 (15)	0.0191 (15)	−0.0151 (14)
O3	0.0551 (17)	0.0440 (15)	0.086 (2)	0.0229 (13)	0.0232 (16)	0.0184 (15)
N1	0.0483 (18)	0.0340 (16)	0.0365 (18)	0.0116 (13)	0.0072 (14)	0.0055 (13)
N2	0.066 (2)	0.0410 (18)	0.0357 (19)	0.0174 (16)	0.0061 (15)	0.0073 (15)
N3	0.066 (2)	0.0388 (18)	0.039 (2)	0.0180 (16)	0.0023 (16)	0.0025 (15)
N4	0.085 (3)	0.0343 (18)	0.055 (3)	0.0153 (17)	0.015 (2)	0.0023 (17)
N5	0.0462 (17)	0.0356 (17)	0.043 (2)	0.0120 (14)	0.0109 (14)	0.0056 (14)
C1	0.112 (5)	0.058 (3)	0.072 (4)	0.038 (3)	−0.007 (3)	0.002 (3)
C2	0.072 (3)	0.039 (2)	0.053 (3)	0.025 (2)	0.008 (2)	0.0082 (19)
C3	0.074 (3)	0.034 (2)	0.039 (2)	0.0078 (19)	0.018 (2)	0.0034 (17)
C4	0.052 (2)	0.040 (2)	0.045 (2)	0.0105 (17)	0.0177 (17)	0.0030 (17)
C5	0.0447 (19)	0.0314 (17)	0.044 (2)	0.0133 (15)	0.0111 (16)	0.0040 (15)
C6	0.045 (2)	0.0347 (19)	0.040 (2)	0.0141 (16)	0.0064 (17)	0.0046 (17)
C7	0.067 (3)	0.049 (2)	0.035 (2)	0.021 (2)	0.0065 (19)	0.0053 (19)
C8	0.050 (2)	0.038 (2)	0.048 (3)	0.0173 (17)	0.0063 (18)	0.0025 (18)
C9	0.045 (2)	0.039 (2)	0.039 (2)	0.0165 (16)	0.0044 (16)	0.0043 (16)
C10	0.0394 (19)	0.040 (2)	0.039 (2)	0.0143 (16)	0.0095 (16)	0.0091 (17)
C11	0.0387 (19)	0.0397 (19)	0.040 (2)	0.0111 (16)	0.0116 (16)	0.0051 (16)
C12	0.048 (2)	0.043 (2)	0.049 (3)	0.0150 (17)	0.0143 (18)	0.0099 (18)
C13	0.054 (2)	0.062 (3)	0.048 (3)	0.018 (2)	0.018 (2)	0.020 (2)
C14	0.050 (2)	0.063 (3)	0.042 (2)	0.008 (2)	0.0156 (19)	0.005 (2)
C15	0.059 (3)	0.051 (2)	0.052 (3)	0.0171 (19)	0.020 (2)	0.002 (2)
C16	0.055 (2)	0.051 (2)	0.042 (2)	0.0219 (19)	0.0118 (18)	0.0064 (18)
C17	0.081 (3)	0.102 (4)	0.047 (3)	0.023 (3)	0.016 (2)	0.001 (3)
O4	0.0562 (19)	0.068 (2)	0.093 (3)	−0.0004 (17)	0.0064 (18)	0.029 (2)
O5	0.086 (2)	0.0397 (15)	0.0366 (16)	0.0298 (14)	0.0064 (14)	0.0063 (12)
O6	0.0470 (14)	0.0376 (13)	0.0424 (15)	0.0119 (11)	0.0075 (12)	0.0120 (12)
N6	0.0492 (17)	0.0314 (15)	0.0333 (17)	0.0138 (13)	0.0108 (13)	0.0039 (13)
N7	0.065 (2)	0.0362 (17)	0.0339 (18)	0.0168 (15)	0.0098 (15)	0.0020 (14)
N8	0.060 (2)	0.0368 (18)	0.044 (2)	0.0155 (15)	0.0099 (16)	0.0006 (15)
N9	0.065 (2)	0.0350 (18)	0.049 (2)	0.0177 (16)	0.0172 (18)	0.0046 (16)
N10	0.0448 (17)	0.0340 (16)	0.0399 (19)	0.0129 (13)	0.0098 (14)	0.0051 (13)
C18	0.058 (3)	0.054 (3)	0.066 (3)	0.009 (2)	0.015 (2)	0.020 (2)
C19	0.058 (2)	0.0299 (17)	0.037 (2)	0.0134 (16)	0.0098 (17)	0.0085 (15)
C20	0.055 (2)	0.0338 (18)	0.034 (2)	0.0196 (16)	0.0113 (17)	0.0053 (15)
C21	0.047 (2)	0.042 (2)	0.043 (2)	0.0215 (16)	0.0103 (17)	0.0077 (17)
C22	0.050 (2)	0.0331 (19)	0.036 (2)	0.0155 (16)	0.0153 (16)	0.0077 (15)
C23	0.043 (2)	0.0366 (19)	0.038 (2)	0.0147 (16)	0.0115 (16)	0.0057 (17)
C24	0.075 (3)	0.043 (2)	0.039 (2)	0.021 (2)	0.011 (2)	0.0041 (18)

C25	0.041 (2)	0.0349 (19)	0.047 (2)	0.0126 (15)	0.0130 (17)	0.0060 (17)
C26	0.0433 (19)	0.0321 (18)	0.040 (2)	0.0118 (15)	0.0125 (16)	0.0043 (15)
C27	0.042 (2)	0.038 (2)	0.035 (2)	0.0134 (16)	0.0122 (16)	0.0085 (16)
C28	0.044 (2)	0.0384 (19)	0.037 (2)	0.0178 (16)	0.0091 (16)	0.0068 (16)
C29	0.051 (2)	0.045 (2)	0.046 (2)	0.0167 (17)	0.0183 (18)	0.0121 (18)
C30	0.062 (3)	0.064 (3)	0.042 (3)	0.023 (2)	0.023 (2)	0.017 (2)
C31	0.062 (3)	0.066 (3)	0.038 (2)	0.033 (2)	0.014 (2)	0.008 (2)
C32	0.058 (2)	0.046 (2)	0.041 (2)	0.0157 (19)	0.0072 (19)	−0.0026 (18)
C33	0.051 (2)	0.044 (2)	0.041 (2)	0.0163 (17)	0.0142 (17)	0.0069 (17)
C34	0.104 (4)	0.103 (4)	0.036 (3)	0.047 (4)	0.018 (3)	0.000 (3)
O7	0.068 (2)	0.0545 (19)	0.066 (2)	0.0063 (16)	0.0117 (16)	0.0164 (17)

Geometric parameters (Å, º)

O1—C1	1.375 (7)	O4—C18	1.417 (6)
O2—C3	1.429 (5)	O5—C20	1.421 (4)
O3—C5	1.424 (5)	O6—C22	1.433 (5)
O3—C2	1.440 (5)	O6—C19	1.438 (4)
N1—C6	1.381 (5)	N6—C23	1.379 (5)
N1—C10	1.385 (5)	N6—C27	1.400 (5)
N1—C5	1.454 (4)	N6—C22	1.456 (5)
N2—C7	1.328 (5)	N7—C24	1.329 (5)
N2—C6	1.350 (5)	N7—C23	1.332 (5)
N3—C7	1.329 (6)	N8—C25	1.341 (5)
N3—C8	1.352 (6)	N8—C24	1.344 (5)
N4—C8	1.347 (6)	N9—C25	1.364 (5)
N5—C10	1.315 (5)	N10—C27	1.323 (5)
N5—C9	1.378 (5)	N10—C26	1.377 (5)
C1—C2	1.515 (7)	C18—C19	1.497 (7)
C2—C3	1.504 (7)	C19—C20	1.517 (5)
C3—C4	1.532 (6)	C20—C21	1.513 (6)
C4—C5	1.519 (6)	C21—C22	1.532 (5)
C6—C9	1.373 (5)	C23—C26	1.382 (5)
C8—C9	1.409 (6)	C25—C26	1.393 (5)
C10—C11	1.472 (6)	C27—C28	1.456 (6)
C11—C12	1.384 (6)	C28—C33	1.392 (5)
C11—C16	1.396 (6)	C28—C29	1.393 (6)
C12—C13	1.381 (6)	C29—C30	1.385 (6)
C13—C14	1.384 (7)	C30—C31	1.374 (6)
C14—C15	1.391 (7)	C31—C32	1.384 (6)
C14—C17	1.507 (7)	C31—C34	1.515 (7)
C15—C16	1.389 (6)	C32—C33	1.386 (6)
C5—O3—C2	109.4 (3)	C22—O6—C19	109.1 (3)
C6—N1—C10	105.9 (3)	C23—N6—C27	105.6 (3)
C6—N1—C5	128.4 (3)	C23—N6—C22	128.1 (3)
C10—N1—C5	125.7 (3)	C27—N6—C22	126.3 (3)
C7—N2—C6	111.0 (3)	C24—N7—C23	111.0 (3)

C7—N3—C8	118.3 (4)	C25—N8—C24	116.8 (3)
C10—N5—C9	104.8 (3)	C27—N10—C26	104.8 (3)
O1—C1—C2	112.7 (4)	O4—C18—C19	109.7 (4)
O3—C2—C3	104.9 (3)	O6—C19—C18	109.7 (3)
O3—C2—C1	104.4 (4)	O6—C19—C20	103.1 (3)
C3—C2—C1	117.3 (5)	C18—C19—C20	114.2 (3)
O2—C3—C2	107.1 (4)	O5—C20—C21	114.2 (3)
O2—C3—C4	109.9 (4)	O5—C20—C19	111.7 (3)
C2—C3—C4	103.0 (3)	C21—C20—C19	101.8 (3)
C5—C4—C3	100.3 (3)	C20—C21—C22	103.9 (3)
O3—C5—N1	109.0 (3)	O6—C22—N6	107.4 (3)
O3—C5—C4	107.9 (3)	O6—C22—C21	106.0 (3)
N1—C5—C4	117.1 (3)	N6—C22—C21	115.5 (3)
N2—C6—C9	125.9 (4)	N7—C23—N6	127.9 (3)
N2—C6—N1	128.3 (3)	N7—C23—C26	126.1 (3)
C9—C6—N1	105.8 (3)	N6—C23—C26	106.1 (3)
N2—C7—N3	129.7 (4)	N7—C24—N8	129.8 (4)
N4—C8—N3	118.9 (4)	N8—C25—N9	119.3 (4)
N4—C8—C9	123.5 (4)	N8—C25—C26	119.1 (3)
N3—C8—C9	117.5 (4)	N9—C25—C26	121.6 (4)
C6—C9—N5	111.0 (3)	N10—C26—C23	111.2 (3)
C6—C9—C8	117.6 (4)	N10—C26—C25	131.7 (3)
N5—C9—C8	131.3 (4)	C23—C26—C25	117.1 (3)
N5—C10—N1	112.4 (3)	N10—C27—N6	112.3 (3)
N5—C10—C11	123.6 (3)	N10—C27—C28	122.9 (3)
N1—C10—C11	123.9 (3)	N6—C27—C28	124.7 (3)
C12—C11—C16	118.4 (4)	C33—C28—C29	118.7 (4)
C12—C11—C10	118.7 (4)	C33—C28—C27	123.2 (3)
C16—C11—C10	122.8 (4)	C29—C28—C27	118.1 (3)
C13—C12—C11	120.7 (4)	C30—C29—C28	120.2 (4)
C12—C13—C14	121.5 (4)	C31—C30—C29	121.2 (4)
C13—C14—C15	117.9 (4)	C30—C31—C32	118.8 (4)
C13—C14—C17	121.5 (5)	C30—C31—C34	121.5 (4)
C15—C14—C17	120.6 (5)	C32—C31—C34	119.8 (4)
C16—C15—C14	121.0 (4)	C31—C32—C33	120.9 (4)
C15—C16—C11	120.4 (4)	C32—C33—C28	120.2 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···N8^{i}	0.82	2.14	2.943 (5)	168
O2—H2*O*···O7^{ii}	0.82	1.93	2.743 (5)	172
C1—H1*A*···N2	0.97	2.69	3.557 (7)	149
C4—H4*A*···N2	0.97	2.37	3.099 (5)	131
C16—H16···O3	0.93	2.49	3.257 (5)	140
C7—H7···N7^{i}	0.93	2.66	3.374 (6)	135
N4—H40*N*···O1^{iii}	0.91 (3)	2.27 (4)	3.033 (6)	142 (4)
N4—H4*N*···O7^{iv}	0.92 (3)	2.05 (3)	2.955 (6)	166 (5)

O4—H4*O*···N9$^{\mathrm{v}}$	0.82	2.22	3.039 (5)	175
O5—H5*O*···N3$^{\mathrm{vi}}$	0.82	2.00	2.805 (4)	166
C20—H20···N7	0.98	2.56	3.201 (5)	123
C21—H21*B*···N7	0.97	2.47	2.992 (5)	113
C32—H32···O1$^{\mathrm{iii}}$	0.93	2.65	3.572 (6)	171
C33—H33···O6	0.93	2.50	3.288 (5)	143
N9—H9*N*···O5$^{\mathrm{ii}}$	0.92 (3)	2.01 (3)	2.903 (5)	164 (4)
O7—H7*O*···N5$^{\mathrm{vii}}$	0.98 (5)	1.87 (6)	2.789 (4)	154 (6)
O7—H70*O*···O4$^{\mathrm{vii}}$	0.99 (5)	1.82 (6)	2.761 (5)	159 (7)
O4—H4*O*···N9	0.82	2.22	3.039 (5)	175

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