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Supramolecular architecture in a co-crystal of the N(7)—H tautomeric form of N^6-benzoyladenine with adipic acid (1/0.5)

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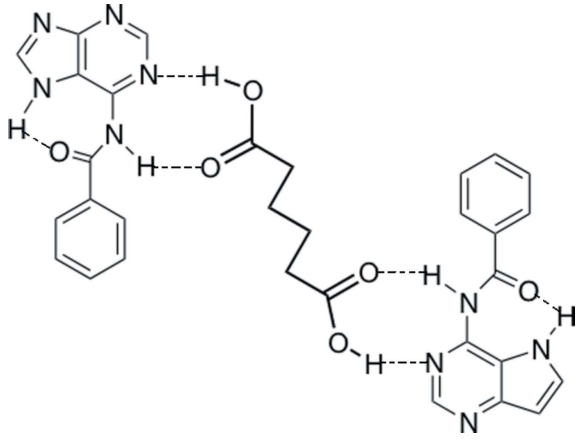
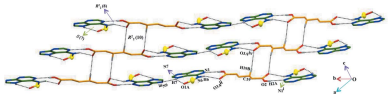
The asymmetric unit of the title co-crystal, $C_{12}H_9N_5O{\cdot}0.5C_6H_{10}O_4$, consists of one molecule of N^6-benzoyladenine (BA) and one half-molecule of adipic acid (AA), the other half being generated by inversion symmetry. The dihedral angle between the adenine and phenyl ring planes is 26.71 (7)°. The N^6-benzoyladenine molecule crystallizes in the N(7)—H tautomeric form with three non-protonated N atoms. This tautomeric form is stabilized by intramolecular N—H···O hydrogen bonding between the carbonyl (C=O) group and the N(7)—H hydrogen atom on the Hoogsteen face of the purine ring, forming an $S(7)$ ring motif. The two carboxyl groups of adipic acid interact with the Watson–Crick face of the BA molecules through O—H···N and N—H···O hydrogen bonds, generating an $R_2^2(8)$ ring motif. The latter units are linked by N—H···N hydrogen bonds, forming layers parallel to $(10\bar{5})$. A weak C—H···O hydrogen bond is also present, linking adipic acid molecules in neighbouring layers, enclosing $R^2_2(10)$ ring motifs and forming a three-dimensional structure. C=O···π and C—H···π interactions are also present in the structure.

1. Chemical context

Adipic acid has been widely used in controlled-release formulations of many drugs and food additives (Roew *et al.*, 2009). N^6-benzoyladenine is a synthetic analogue of a group of naturally occurring N^6-substituted adenines having plant-growth-stimulating activity (cytokinins) (McHugh & Erxleben, 2011). A number of co-crystals involving adipic acid have been reported in the literature (Lemmerer *et al.*, 2012; Lin *et al.*, 2012; Matulková *et al.*, 2014; Thanigaimani *et al.*, 2012). This paper deals with a co-crystal formed between N^6-benzoyladenine and adipic acid (I).





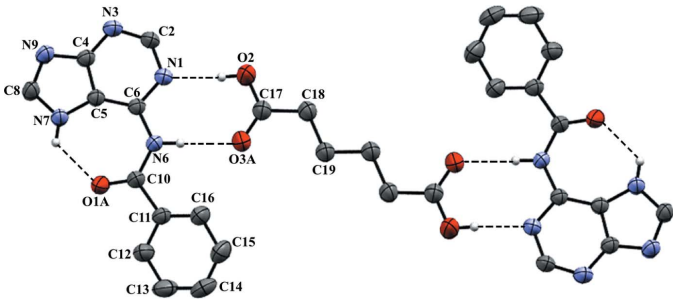


Figure 1
A *Mercury* (Macrae *et al.*, 2008) view of the title compound (I), showing the atom-numbering scheme. Disordered oxygen atoms are omitted for clarity. H atoms not involved in hydrogen bonding have been omitted for clarity. Unlabelled atoms are related by the symmetry operation $1 - x$, $1 - y$, $-z$.

2. Structural commentary

The asymmetric unit of (I) contains one N^6-benzoyladenine (BA) molecule and a half-molecule of adipic acid (AA). As evident from the angles at N7 [C8—N7—C5 = 106.82 (11)°] and N9 [C8—N9—C4 = 103.90 (11)°], the N^6-benzoyladenine moiety exists in the N(7)—H tautomeric form with non-protonated N1, N3 and N9 atoms. In addition, the C8—N7 bond [1.3415 (17) Å)] is longer than C8—N9 [1.3175 (19) Å]. These values are similar to those in neutral N^6-benzoyladenine (Raghunathan & Pattabhi, 1981). An intramolecular hydrogen bond in the Hoogsteen face between N7—H7 and the benzoyl oxygen atom O1 forms a $S(7)$ ring motif. The dihedral angle between the adenine and phenyl ring plane is 26.71 (7)° and the C6—N6—C10—C11 torsion angle is 173.08 (14)°. The bond lengths and bond angles of AA are in the range of values reported (Srinivasa Gopalan *et al.*, 1999; 2000). The values for the torsion angles C18—C19—C19a—C18a [180.00 (13)°] and C17—C18—C19—C19a [–176.09 (14)°] indicate that the carbon chain of AA is fully extended.

In the crystal structures of N^6-benzyladenine (Raghunathan & Pattabhi, 1981), N^6-furfuryladenine (Soriano-Garcia & Parthasarathy, 1977), N^6-benzyladenine hydrobromide (Umadevi *et al.*, 2001), N^6-furfuryladenine hydrochloride (Stanley *et al.*, 2003), N^6-benzyladeninium *p*-toluenesulfonate (Tamilselvi & Muthiah, 2011), N^6-benzyladeninium nitrate, N^6-benzyladeninium 3-hydroxy picolinate (Nirmalram *et al.*, 2011) and the hydrate adduct of N^6-benzyladenine-5-sulfosalicylic acid (Xia *et al.*, 2010), the N^6-substituent is distal to the N7 position, whereas in the crystal structures of N^6-benzoyladenine (Raghunathan *et al.*, 1983), N^6-benzoyladenine-3-hydroxypyridinium-2-carboxylate (1:1), N^6-benzoyladenine-DL-tartaric acid (1:1) (Karthikeyan *et al.*, 2015), N^6-benzyladeninium nitrate (Karthikeyan *et al.*, 2015) and the title compound, the N^6-substituent is distal to N1 and *syn* to adenine nitrogen atom N7. In the present structure, this may be attributed to the presence of the N7—H7···O1*A* intramolecular hydrogen bond (Table 1).

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

Cg is the centroid of the C11–C16 phenyl ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*A*···N1^{i}	0.82	1.92	2.7327 (19)	175
N6—H6···O3*A*^{ii}	0.86	2.09	2.904 (11)	157
N7—H7···O1*A*	0.86	2.04	2.616 (16)	124
N7—H7···N9^{iii}	0.86	2.17	2.9271 (17)	146
C19—H19*B*···O3*A*^{iv}	0.97	2.54	3.481 (11)	164
C2—H2···*Cg*3^{v}	0.93	2.94	3.4611 (16)	117

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

3. Supramolecular features

Each of the two carboxyl groups of adipic acid interacts with the Watson–Crick face (atoms N1 and N6) of the corresponding BA through O—H···N and N—H···O hydrogen bonds, generating an $R_2^2(8)$ ring motif (Fig. 1). Thus each adipic acid molecule bridges two BA molecules. The latter units are linked by N7—H7···N9^{iii} hydrogen bonds (Table 1) forming layers parallel to plane (10$\bar{5}$). A weak C—H···O hydrogen bond (C19—H19*B*···O3*A*^{iv}) is also present (Table 1 and Fig. 2), linking adipic acid molecules in neighbouring layers, enclosing $R_2^2(10)$ ring motifs and forming a three-dimensional structure. Thus atom O3*A* functions as a bifurcated hydrogen-bond acceptor whereas N7—H is a bifurcated hydrogen-bond donor.

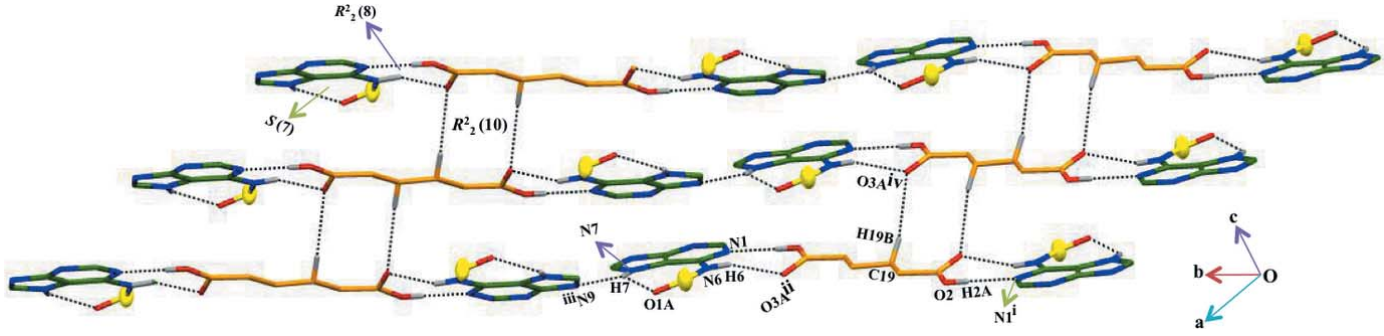


Figure 2
A view of the sheet-like supramolecular architecture generated *via* C19—H19*B*···O3*A* hydrogen bonds (black dotted lines). Phenyl rings are indicated as yellow balls. H atoms not involved in hydrogen bonding have been omitted for clarity. Symmetry codes are as given in Table 1.

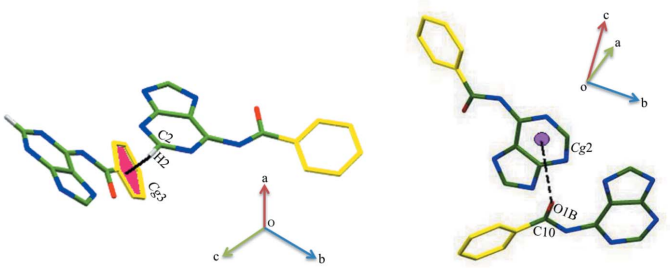


Figure 3
(*a*) A view of the C—H···π interaction in compound (I). *Cg*3 is the centroid of the phenyl ring of the BA molecule (symmetry code: $x, -1+y, z$). (*b*) A view of the C═O···π interaction. *Cg*2 is the centroid of the pyrimidine ring of the BA molecule (symmetry code: $1-x, \frac{1}{2}+y, \frac{1}{2}-z$).

The crystal structure also features C2—H2···π interactions between purine and phenyl rings (Fig. 3*a*) and C10═O1*B*···π interactions between the carbonyl oxygen O1*B* and the centroid of the (N1/C2/N3/C4/C5/C6) pyrimidine ring [O···centroid = 3.407 (10) Å; symmetry code: $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; Fig. 3*b*] (Safaei-Ghomi *et al.*, 2009).

4. Database survey

The neutral molecule N^6-benzoyladenine was reported by Raghunathan & Pattabhi (1981). Co-crystals have also been reported: N^6-benzoyladenine-3-hydroxypyridinium-2-carboxylate (1:1), N^6-benzoyladenine-DL-tartaric acid (1:1) (Karthikeyan *et al.*, 2015) and N^6-benzoyladeninium nitrate (Karthikeyan *et al.*, 2016). Similarly, co-crystals of adipic acid with pyrimidine derivatives [adenine (Byres *et al.*, 2009), caffeine (Bučar *et al.*, 2007), cytosine (Das & Baruah, 2011), bis-pyrimidine-amine-linked xylene spacer (Goswami *et al.*, 2010)] have also been reported.

5. Synthesis and crystallization

The title co-crystal was synthesized by mixing a DMF solution of N^6-benzoyladenine (30 mg) and adipic acid (19 mg) (total volume = 10 mL). The mixture was warmed in a water bath for 20 min. After cooling to room temperature, colourless plate-like crystals were collected from the mother liquor after a few days (m.p. 438 K).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Atoms O1 and O3 are disordered over two positions with refined occupancy ratios of 0.57 (3):0.43 (3) and 0.63 (3):0.37 (3), respectively. Hydrogen atoms were readily located in difference Fourier maps and were subsequently treated as riding atoms in geometrically idealized positions, with C—H = 0.93 (aromatic) or 0.97 (methylene), N—H = 0.86, and O—H = 0.82 Å, and with U_{iso}(H) = kU_{eq}(C,N,O), where k = 1.5 for hydroxy and 1.2 for all other H atoms.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_9N_5O{\cdot}0.5C_6H_{10}O_4$
M_r	312.31
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	6.1776 (4), 9.2296 (4), 25.7480 (15)
β (°)	97.117 (6)
V (Å^3)	1456.76 (14)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.60 × 0.60 × 0.40
Data collection	
Diffractometer	Agilent SuperNova Dual Source diffractometer with an Atlas detector
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2013)
T_{min}, T_{max}	0.756, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9480, 3325, 2755
R_{int}	0.020
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.122, 1.05
No. of reflections	3325
No. of parameters	230
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.25, −0.22

Computer programs: *CrysAlis PRO* (Agilent, 2013), *SUPERFLIP* (Palatinus & Chapuis, 2007), *SHELXL2014* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008).

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Acta Cryst. (2016). E**72**, 805-808 [https://doi.org/10.1107/S2056989016007581]

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO* (Agilent, 2013); data reduction: *CrysAlis PRO* (Agilent, 2013); program(s) used to solve structure: SUPERFLIP (Palatinus & Chapuis, 2007); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *PLATON* (Spek, 2009).

N^6-Benzoyladenine–adipic acid (1/0.5)

Crystal data

$C_{12}H_9N_5O{\cdot}0.5C_6H_{10}O_4$
M_r = 312.31
Monoclinic, $P2_1/c$
a = 6.1776 (4) Å
b = 9.2296 (4) Å
c = 25.7480 (15) Å
β = 97.117 (6)°
V = 1456.76 (14) Å^3
Z = 4
$F(000)$ = 652
D_x = 1.424 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4139 reflections
θ = 3.3–30.1°
μ = 0.10 mm^{-1}
T = 293 K
Prism, colorless
0.60 × 0.60 × 0.40 mm

Data collection

Agilent SuperNova Dual Source diffractometer with an Atlas detector
Radiation source: SuperNova (Mo) X-ray Source
Mirror monochromator
Detector resolution: 10.4933 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2013)
T_{min} = 0.756, T_{max} = 1.000
9480 measured reflections
3325 independent reflections
2755 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 27.5°, θ_{min} = 3.2°
h = −8→7
k = −11→11
l = −33→31

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.122
S = 1.05
3325 reflections
230 parameters
0 restraints
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 0.3295P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Extinction correction: SHELXL2014 (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0130 (18)

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_{iso}*/U_{eq}	Occ. (<1)
O1A	0.7104 (15)	0.6427 (14)	0.1669 (8)	0.094 (4)	0.57 (3)
O1B	0.6582 (19)	0.6621 (6)	0.1877 (4)	0.054 (2)	0.43 (3)
N1	0.3308 (2)	0.27081 (12)	0.16588 (5)	0.0415 (3)	
N3	0.5648 (2)	0.09828 (13)	0.21438 (5)	0.0477 (3)	
N6	0.39990 (19)	0.51100 (12)	0.15270 (5)	0.0391 (3)	
H6	0.2702	0.5109	0.1361	0.047*	
N7	0.85319 (19)	0.42515 (12)	0.22672 (5)	0.0402 (3)	
H7	0.8790	0.5157	0.2226	0.048*	
N9	0.9054 (2)	0.19667 (13)	0.25397 (5)	0.0470 (3)	
C2	0.3848 (3)	0.13827 (15)	0.18545 (6)	0.0468 (4)	
H2	0.2811	0.0660	0.1774	0.056*	
C4	0.7054 (2)	0.20808 (14)	0.22480 (5)	0.0389 (3)	
C5	0.6683 (2)	0.35149 (13)	0.20707 (5)	0.0352 (3)	
C6	0.4717 (2)	0.38085 (13)	0.17619 (5)	0.0347 (3)	
C8	0.9855 (3)	0.32896 (15)	0.25376 (6)	0.0451 (4)	
H8	1.1219	0.3535	0.2709	0.054*	
C10	0.5100 (3)	0.63803 (16)	0.15283 (7)	0.0493 (4)	
C11	0.4104 (2)	0.75951 (14)	0.11985 (6)	0.0412 (3)	
C12	0.5550 (3)	0.86137 (17)	0.10534 (7)	0.0544 (4)	
H12	0.7028	0.8527	0.1173	0.065*	
C13	0.4831 (3)	0.97575 (19)	0.07333 (8)	0.0627 (5)	
H13	0.5825	1.0423	0.0630	0.075*	
C14	0.2660 (3)	0.99109 (19)	0.05686 (7)	0.0628 (5)	
H14	0.2168	1.0681	0.0353	0.075*	
C15	0.1208 (3)	0.8931 (2)	0.07213 (8)	0.0655 (5)	
H15	−0.0274	0.9047	0.0611	0.079*	
C16	0.1909 (3)	0.77622 (18)	0.10389 (7)	0.0538 (4)	
H16	0.0908	0.7102	0.1142	0.065*	
O2	0.9399 (2)	0.25032 (13)	0.10377 (6)	0.0694 (4)	
H2A	1.0565	0.2620	0.1223	0.104*	
O3A	1.0228 (15)	0.4644 (11)	0.0753 (5)	0.072 (2)	0.63 (3)
O3B	0.951 (3)	0.4828 (6)	0.0985 (9)	0.070 (5)	0.37 (3)
C17	0.8870 (3)	0.36824 (17)	0.07825 (6)	0.0494 (4)	
C18	0.6762 (3)	0.36172 (16)	0.04285 (6)	0.0491 (4)	
H18A	0.5619	0.3312	0.0631	0.059*	

H18B	0.6882	0.2888	0.0162	0.059*
C19	0.6100 (3)	0.50345 (16)	0.01626 (6)	0.0494 (4)
H19A	0.6069	0.5781	0.0427	0.059*
H19B	0.7188	0.5308	−0.0060	0.059*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1A	0.047 (3)	0.085 (4)	0.138 (8)	−0.023 (2)	−0.033 (4)	0.071 (4)
O1B	0.052 (3)	0.028 (2)	0.073 (4)	−0.0097 (15)	−0.024 (2)	0.011 (2)
N1	0.0423 (6)	0.0333 (6)	0.0467 (7)	−0.0045 (5)	−0.0037 (5)	0.0046 (5)
N3	0.0559 (8)	0.0299 (6)	0.0536 (7)	−0.0047 (5)	−0.0074 (6)	0.0067 (5)
N6	0.0365 (6)	0.0308 (6)	0.0470 (6)	0.0002 (4)	−0.0071 (5)	0.0062 (5)
N7	0.0399 (6)	0.0269 (5)	0.0503 (7)	0.0015 (5)	−0.0079 (5)	0.0000 (5)
N9	0.0495 (7)	0.0310 (6)	0.0561 (7)	0.0051 (5)	−0.0108 (6)	0.0036 (5)
C2	0.0519 (9)	0.0325 (7)	0.0528 (8)	−0.0091 (6)	−0.0060 (7)	0.0062 (6)
C4	0.0444 (8)	0.0292 (6)	0.0412 (7)	0.0023 (5)	−0.0023 (6)	0.0017 (5)
C5	0.0381 (7)	0.0280 (6)	0.0383 (7)	0.0015 (5)	−0.0002 (6)	−0.0008 (5)
C6	0.0380 (7)	0.0290 (6)	0.0362 (6)	0.0006 (5)	0.0007 (6)	0.0015 (5)
C8	0.0423 (8)	0.0341 (7)	0.0550 (8)	0.0045 (6)	−0.0101 (7)	−0.0007 (6)
C10	0.0461 (8)	0.0357 (7)	0.0611 (9)	−0.0047 (6)	−0.0131 (7)	0.0124 (7)
C11	0.0472 (8)	0.0303 (6)	0.0441 (7)	0.0017 (6)	−0.0019 (6)	0.0044 (5)
C12	0.0510 (9)	0.0398 (8)	0.0710 (11)	−0.0011 (7)	0.0017 (8)	0.0131 (7)
C13	0.0716 (12)	0.0437 (9)	0.0746 (12)	0.0012 (8)	0.0155 (10)	0.0202 (8)
C14	0.0809 (13)	0.0479 (9)	0.0590 (10)	0.0163 (9)	0.0061 (9)	0.0205 (8)
C15	0.0542 (10)	0.0617 (11)	0.0771 (12)	0.0142 (9)	−0.0059 (9)	0.0204 (9)
C16	0.0464 (9)	0.0455 (8)	0.0672 (10)	0.0021 (7)	−0.0019 (8)	0.0146 (7)
O2	0.0568 (7)	0.0461 (6)	0.0963 (10)	−0.0026 (5)	−0.0264 (7)	0.0128 (6)
O3A	0.061 (3)	0.072 (2)	0.076 (4)	−0.026 (2)	−0.024 (3)	0.027 (2)
O3B	0.069 (5)	0.037 (2)	0.092 (8)	−0.006 (2)	−0.035 (5)	0.002 (2)
C17	0.0477 (9)	0.0428 (8)	0.0544 (9)	−0.0017 (7)	−0.0073 (7)	0.0029 (7)
C18	0.0472 (8)	0.0408 (8)	0.0558 (9)	−0.0017 (6)	−0.0071 (7)	−0.0016 (7)
C19	0.0481 (9)	0.0411 (8)	0.0554 (9)	−0.0023 (6)	−0.0070 (7)	0.0023 (7)

Geometric parameters (Å, º)

O1A—C10	1.247 (6)	C12—C13	1.378 (2)
O1B—C10	1.221 (6)	C12—H12	0.9300
N1—C6	1.3424 (17)	C13—C14	1.363 (3)
N1—C2	1.3489 (17)	C13—H13	0.9300
N3—C2	1.3125 (19)	C14—C15	1.365 (3)
N3—C4	1.3401 (18)	C14—H14	0.9300
N6—C10	1.3551 (18)	C15—C16	1.390 (2)
N6—C6	1.3926 (16)	C15—H15	0.9300
N6—H6	0.8600	C16—H16	0.9300
N7—C8	1.3415 (17)	O2—C17	1.2923 (18)
N7—C5	1.3712 (17)	O2—H2A	0.8200
N7—H7	0.8601	O3A—C17	1.230 (4)

N9—C8	1.3175 (19)	O3B—C17	1.223 (6)
N9—C4	1.3684 (18)	C17—C18	1.495 (2)
C2—H2	0.9300	C18—C19	1.509 (2)
C4—C5	1.4096 (17)	C18—H18A	0.9700
C5—C6	1.3931 (18)	C18—H18B	0.9700
C8—H8	0.9300	C19—C19^{i}	1.506 (3)
C10—C11	1.4924 (18)	C19—H19A	0.9700
C11—C16	1.376 (2)	C19—H19B	0.9700
C11—C12	1.380 (2)		

C6—N1—C2	119.23 (11)	C13—C12—H12	119.6
C2—N3—C4	112.56 (12)	C11—C12—H12	119.6
C10—N6—C6	127.77 (11)	C14—C13—C12	119.81 (17)
C10—N6—H6	116.0	C14—C13—H13	120.1
C6—N6—H6	116.2	C12—C13—H13	120.1
C8—N7—C5	106.82 (11)	C13—C14—C15	119.86 (15)
C8—N7—H7	126.7	C13—C14—H14	120.1
C5—N7—H7	126.5	C15—C14—H14	120.1
C8—N9—C4	103.90 (11)	C14—C15—C16	121.01 (16)
N3—C2—N1	128.29 (13)	C14—C15—H15	119.5
N3—C2—H2	115.9	C16—C15—H15	119.5
N1—C2—H2	115.9	C11—C16—C15	119.12 (16)
N3—C4—N9	124.79 (12)	C11—C16—H16	120.4
N3—C4—C5	124.74 (12)	C15—C16—H16	120.4
N9—C4—C5	110.47 (12)	C17—O2—H2A	109.5
N7—C5—C6	137.86 (12)	O3B—C17—O2	117.6 (6)
N7—C5—C4	104.56 (11)	O3A—C17—O2	120.5 (3)
C6—C5—C4	117.57 (12)	O3B—C17—C18	120.5 (3)
N1—C6—N6	113.77 (11)	O3A—C17—C18	122.7 (2)
N1—C6—C5	117.61 (11)	O2—C17—C18	114.98 (13)
N6—C6—C5	128.60 (12)	C17—C18—C19	114.09 (13)
N9—C8—N7	114.25 (12)	C17—C18—H18A	108.7
N9—C8—H8	122.9	C19—C18—H18A	108.7
N7—C8—H8	122.9	C17—C18—H18B	108.7
O1B—C10—N6	119.4 (5)	C19—C18—H18B	108.7
O1A—C10—N6	120.7 (5)	H18A—C18—H18B	107.6
O1B—C10—C11	120.0 (3)	C19^{i}—C19—C18	112.99 (16)
O1A—C10—C11	117.6 (3)	C19^{i}—C19—H19A	109.0
N6—C10—C11	118.50 (12)	C18—C19—H19A	109.0
C16—C11—C12	119.33 (13)	C19^{i}—C19—H19B	109.0
C16—C11—C10	125.15 (14)	C18—C19—H19B	109.0
C12—C11—C10	115.52 (13)	H19A—C19—H19B	107.8
C13—C12—C11	120.82 (16)		

C4—N3—C2—N1	0.6 (3)	C6—N6—C10—O1B	−23.5 (8)
C6—N1—C2—N3	−0.5 (3)	C6—N6—C10—O1A	13.7 (14)
C2—N3—C4—N9	−179.85 (15)	C6—N6—C10—C11	173.08 (14)
C2—N3—C4—C5	−0.1 (2)	O1B—C10—C11—C16	−138.8 (8)

C8—N9—C4—N3	179.82 (16)	O1A—C10—C11—C16	−175.5 (14)
C8—N9—C4—C5	0.06 (18)	N6—C10—C11—C16	24.5 (3)
C8—N7—C5—C6	−179.15 (18)	O1B—C10—C11—C12	40.7 (9)
C8—N7—C5—C4	−0.01 (16)	O1A—C10—C11—C12	4.0 (14)
N3—C4—C5—N7	−179.79 (15)	N6—C10—C11—C12	−156.02 (16)
N9—C4—C5—N7	−0.03 (17)	C16—C11—C12—C13	−2.8 (3)
N3—C4—C5—C6	−0.4 (2)	C10—C11—C12—C13	177.68 (17)
N9—C4—C5—C6	179.31 (13)	C11—C12—C13—C14	1.8 (3)
C2—N1—C6—N6	178.40 (13)	C12—C13—C14—C15	0.0 (3)
C2—N1—C6—C5	−0.2 (2)	C13—C14—C15—C16	−0.7 (3)
C10—N6—C6—N1	−175.34 (15)	C12—C11—C16—C15	2.0 (3)
C10—N6—C6—C5	3.0 (3)	C10—C11—C16—C15	−178.52 (16)
N7—C5—C6—N1	179.62 (16)	C14—C15—C16—C11	−0.3 (3)
C4—C5—C6—N1	0.6 (2)	O3B—C17—C18—C19	26.0 (16)
N7—C5—C6—N6	1.3 (3)	O3A—C17—C18—C19	−19.2 (10)
C4—C5—C6—N6	−177.74 (14)	O2—C17—C18—C19	176.05 (16)
C4—N9—C8—N7	−0.08 (19)	C17—C18—C19—C19^{i}	−176.11 (18)
C5—N7—C8—N9	0.06 (19)		

Symmetry code: (i) −*x*+1, −*y*+1, −*z*.

Hydrogen-bond geometry (Å, º)

Cg is the centroid of the C11–C16 phenyl ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*A*···N1^{ii}	0.82	1.92	2.7327 (19)	175
N6—H6···O3*A*^{iii}	0.86	2.09	2.904 (11)	157
N7—H7···O1*A*	0.86	2.04	2.616 (16)	124
N7—H7···N9^{iv}	0.86	2.17	2.9271 (17)	146
C19—H19*B*···O3*A*^{v}	0.97	2.54	3.481 (11)	164
C2—H2···*Cg*3^{vi}	0.93	2.94	3.4611 (16)	117

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