

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

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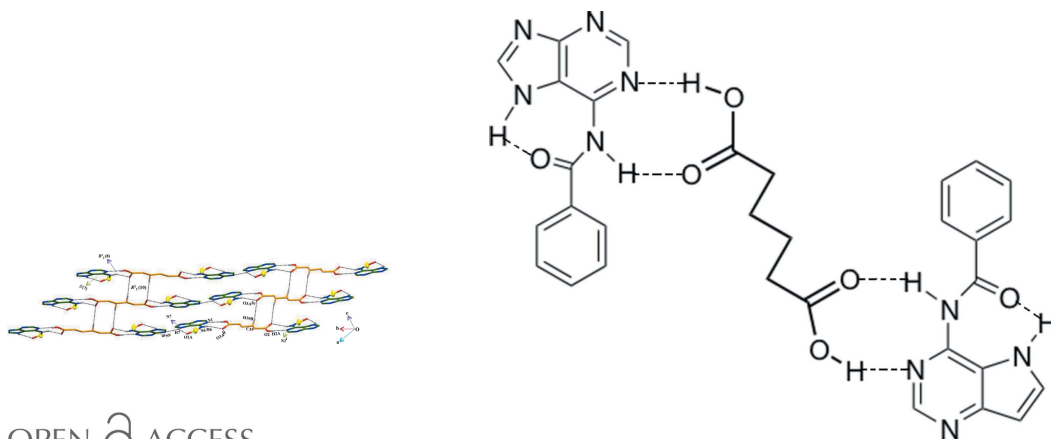
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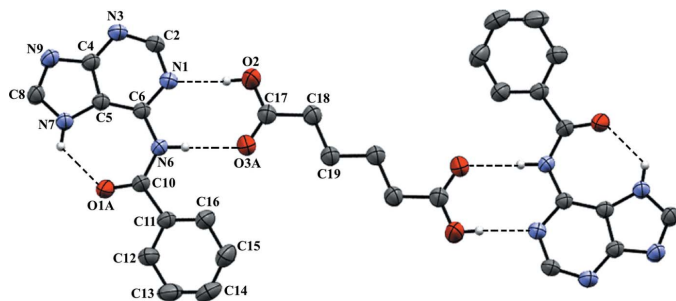
The asymmetric unit of the title co-crystal,  $C_{12}H_9N_5O \cdot 0.5C_6H_{10}O_4$ , consists of one molecule of *N*<sup>6</sup>-benzoyladenine (BA) and one half-molecule of adipic acid (AA), the other half being generated by inversion symmetry. The dihedral angle between the adenine and phenyl ring planes is 26.71 (7)°. The *N*<sup>6</sup>-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 $\cdots$ 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 $\cdots$ N and N—H $\cdots$ O hydrogen bonds, generating an *R*<sub>2</sub><sup>2</sup>(8) ring motif. The latter units are linked by N—H $\cdots$ N hydrogen bonds, forming layers parallel to (10 $\bar{5}$ ). A weak C—H $\cdots$ O hydrogen bond is also present, linking adipic acid molecules in neighbouring layers, enclosing *R*<sub>2</sub><sup>2</sup>(10) ring motifs and forming a three-dimensional structure. C=O $\cdots$  $\pi$  and C—H $\cdots$  $\pi$  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*<sup>6</sup>-benzoyladenine is a synthetic analogue of a group of naturally occurring *N*<sup>6</sup>-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*<sup>6</sup>-benzoyladenine and adipic acid (I).



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**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 [ $C8-N7-C5 = 106.82(11)^\circ$ ] and N9 [ $C8-N9-C4 = 103.90(11)^\circ$ ], 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 [ $1.3415(17) \text{ \AA}$ ] is longer than C8–N9 [ $1.3175(19) \text{ \AA}$ ]. 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  $26.71(7)^\circ$  and the C6–N6–C10–C11 torsion angle is  $173.08(14)^\circ$ . 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 [ $180.00(13)^\circ$ ] and C17–C18–C19–C19a [ $-176.09(14)^\circ$ ] indicate that the carbon chain of AA is fully extended.

In the crystal structures of  $N^6$ -benzoyladenine (Raghunathan & Pattabhi, 1981),  $N^6$ -furfuryladenine (Soriano-Garcia & Parthasarathy, 1977),  $N^6$ -benzoyladenine hydrobromide (Umadevi *et al.*, 2001),  $N^6$ -furfuryladenine hydrochloride (Stanley *et al.*, 2003),  $N^6$ -benzoyladeninium *p*-toluenesulfonate

**Table 1**

Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ ).

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

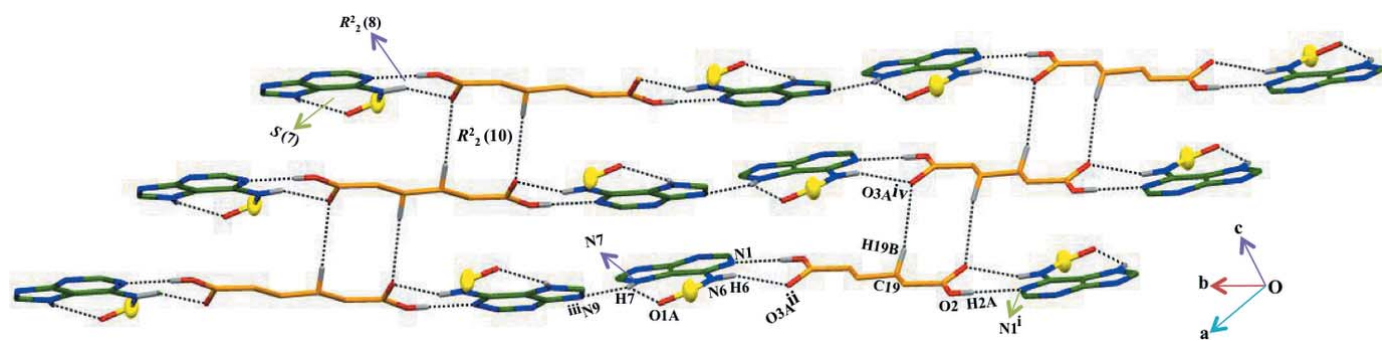
| $D-H \cdots A$             | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|----------------------------|-------|--------------|--------------|----------------|
| $O2-H2A \cdots N1^i$       | 0.82  | 1.92         | 2.7327 (19)  | 175            |
| $N6-H6 \cdots O3A^{ii}$    | 0.86  | 2.09         | 2.904 (11)   | 157            |
| $N7-H7 \cdots O1A$         | 0.86  | 2.04         | 2.616 (16)   | 124            |
| $N7-H7 \cdots N9^{iii}$    | 0.86  | 2.17         | 2.9271 (17)  | 146            |
| $C19-H19B \cdots O3A^{iv}$ | 0.97  | 2.54         | 3.481 (11)   | 164            |
| $C2-H2 \cdots Cg3^v$       | 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)  $x, y-1, z$ .

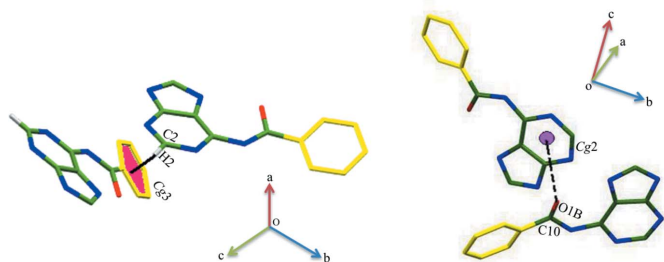
(Tamilselvi & Muthiah, 2011),  $N^6$ -benzoyladeninium nitrate,  $N^6$ -benzoyladeninium 3-hydroxy picolinate (Nirmalram *et al.*, 2011) and the hydrate adduct of  $N^6$ -benzoyladenine-5-sulfosalicylic acid (Xia *et al.*, 2010), the  $N^6$ -substituent is distal to the N7 position, whereas in the crystal 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),  $N^6$ -benzoyladeninium 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 $\cdots$ O1A intramolecular hydrogen bond (Table 1).

## 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 $\cdots$ N and N–H $\cdots$ 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 $\cdots$ N9<sup>iii</sup> hydrogen bonds (Table 1) forming layers parallel to plane (10 $\bar{5}$ ). A weak C–H $\cdots$ O hydrogen bond (C19–H19B $\cdots$ O3A<sup>iv</sup>) 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 O3A 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–H19B $\cdots$ O3A 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 $\cdots\pi$  interaction in compound (I). Cg3 is the centroid of the phenyl ring of the BA molecule (symmetry code:  $x, -1 + y, z$ ). (b) A view of the C=O $\cdots\pi$  interaction. Cg2 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 $\cdots\pi$  interactions between purine and phenyl rings (Fig. 3a) and C10=O1B $\cdots\pi$  interactions between the carbonyl oxygen O1B and the centroid of the (N1/C2/N3/C4/C5/C6) pyrimidine ring [O $\cdots$ centroid = 3.407 (10) Å; symmetry code:  $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; Fig. 3b] (Safaei-Ghomi *et al.*, 2009).

#### 4. Database survey

The neutral molecule *N*<sup>6</sup>-benzoyladenine was reported by Raghunathan & Pattabhi (1981). Co-crystals have also been reported: *N*<sup>6</sup>-benzoyladenine-3-hydroxypyridinium-2-carboxylate (1:1), *N*<sup>6</sup>-benzoyladenine-DL-tartaric acid (1:1) (Karthikeyan *et al.*, 2015) and *N*<sup>6</sup>-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*<sup>6</sup>-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  $U_{\text{iso}}(\text{H}) = kU_{\text{eq}}(\text{C,N,O})$ , where  $k = 1.5$  for hydroxy and 1.2 for all other H atoms.

**Table 2**

Experimental details.

|   |  |
|---|--|
| Crystal data  |  |
| Chemical formula  | C <sub>12</sub> H <sub>9</sub> N <sub>5</sub> O·0.5C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> |
| <i>M</i> <sub>r</sub>   | 312.31   |
| Crystal system, space group   | Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>   |
| Temperature (K)   | 293  |
| <i>a</i> , <i>b</i> , <i>c</i> (Å)  | 6.1776 (4), 9.2296 (4), 25.7480 (15)   |
| $\beta$ (°)   | 97.117 (6)   |
| <i>V</i> (Å <sup>3</sup> )  | 1456.76 (14)   |
| <i>Z</i>  | 4  |
| Radiation type  | Mo <i>K</i> $\alpha$   |
| $\mu$ (mm <sup>-1</sup> )   | 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 ( <i>CrysAlis PRO</i> ; Agilent, 2013)  |
| <i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>   | 0.756, 1.000   |
| No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections                             | 9480, 3325, 2755   |
| <i>R</i> <sub>int</sub>   | 0.020  |
| ( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )   | 0.649  |
| Refinement  |  |
| <i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i> | 0.045, 0.122, 1.05   |
| No. of reflections  | 3325   |
| No. of parameters   | 230  |
| H-atom treatment  | H-atom parameters constrained  |
| $\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )  | 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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#### References

- Agilent (2013). *CrysAlis PRO*. Agilent Technologies UK Ltd, Yarnton, England.
- Bučar, D. K., Henry, R. F., Lou, X., Borchardt, T. & Zhang, G. G. Z. (2007). *Chem. Commun.* pp. 525–527.
- Byres, M., Cox, P. J., Kay, G. & Nixon, E. (2009). *CrystEngComm*, **11**, 135–142.
- Das, B. & Baruah, J. B. (2011). *J. Mol. Struct.* **1001**, 134–138.
- Goswami, S., Hazra, A. & Fun, H.-K. (2010). *J. Incl. Phenom. Macrocycl. Chem.* **68**, 461–466.
- Karthikeyan, A., Jeeva Jasmine, N., Thomas Muthiah, P. & Perdih, F. (2016). *Acta Cryst.* **E72**, 140–143.
- Karthikeyan, A., Swinton Darius, R., Thomas Muthiah, P. & Perdih, F. (2015). *Acta Cryst.* **C71**, 985–990.
- Lemmer, A., Bernstein, J. & Kahlenberg, V. (2012). *Acta Cryst.* **E68**, o190.
- Lin, S., Jia, R., Gao, F. & Zhou, X. (2012). *Acta Cryst.* **E68**, o3457.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

- Matulková, I., Císařová, I., Němec, I. & Fábry, J. (2014). *Acta Cryst.* **C70**, 927–933.
- McHugh, C. & Erxleben, A. (2011). *Cryst. Growth Des.* **11**, 5096–5104.
- Nirmalram, J. S., Tamilselvi, D. & Muthiah, P. T. (2011). *J. Chem. Crystallogr.* **41**, 864–867.
- Palatinus, L. & Chapuis, G. (2007). *J. Appl. Cryst.* **40**, 786–790.
- Raghunathan, S. & Pattabhi, V. (1981). *Acta Cryst.* **B37**, 1670–1673.
- Raghunathan, S., Sinha, B. K., Pattabhi, V. & Gabe, E. J. (1983). *Acta Cryst.* **C39**, 1545–1547.
- Roew, R., Sheskey, P. & Quinn, M. (2009). *Adipic Acid, Handbook of Pharmaceutical Excipients*, pp. 11–12.
- Safaei-Ghomi, J., Aghabozorg, H., Motyeian, E. & Ghadermazi, M. (2009). *Acta Cryst.* **E65**, m2–m3.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Soriano-Garcia, M. & Parthasarathy, R. (1977). *Acta Cryst.* **B33**, 2674–2677.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Srinivasa Gopalan, R., Kumaradhas, P. & Kulkarni, G. U. (1999). *J. Solid State Chem.* **148**, 129–134.
- Srinivasa Gopalan, R., Kumaradhas, P., Kulkarni, G. U. & Rao, C. N. R. (2000). *J. Mol. Struct.* **521**, 97–106.
- Stanley, N., Muthiah, P. T. & Geib, S. J. (2003). *Acta Cryst.* **C59**, o27–o29.
- Tamilselvi, D. & Muthiah, P. T. (2011). *Acta Cryst.* **C67**, o192–o194.
- Thanigaimani, K., Razak, I. A., Arshad, S., Jagatheesan, R. & Santhanaraj, K. J. (2012). *Acta Cryst.* **E68**, o2938–o2939.
- Umadevi, B., Stanley, N., Muthiah, P. T., Bocelli, G. & Cantoni, A. (2001). *Acta Cryst.* **E57**, o881–o883.
- Xia, M., Ma, K. & Zhu, Y. (2010). *J. Chem. Crystallogr.* **40**, 634–638.

## supporting information

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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<sup>6</sup>-Benzoyladenine–adipic acid (1/0.5)

#### Crystal data

C<sub>12</sub>H<sub>9</sub>N<sub>5</sub>O·0.5C<sub>6</sub>H<sub>10</sub>O<sub>4</sub>

*M<sub>r</sub>* = 312.31

Monoclinic, *P*2<sub>1</sub>/*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<sup>3</sup>

*Z* = 4

*F*(000) = 652

*D<sub>x</sub>* = 1.424 Mg m<sup>-3</sup>

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 4139 reflections

θ = 3.3–30.1°

μ = 0.10 mm<sup>-1</sup>

*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<sup>-1</sup>

ω scans

Absorption correction: multi-scan  
(*CrysAlis PRO*; Agilent, 2013)

*T<sub>min</sub>* = 0.756, *T<sub>max</sub>* = 1.000

9480 measured reflections

3325 independent reflections

2755 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.020

θ<sub>max</sub> = 27.5°, θ<sub>min</sub> = 3.2°

*h* = -8→7

*k* = -11→11

*l* = -33→31

#### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.045

*wR*(*F*<sup>2</sup>) = 0.122

*S* = 1.05

3325 reflections

230 parameters

0 restraints

Hydrogen site location: mixed

H-atom parameters constrained

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0541*P*)<sup>2</sup> + 0.3295*P*]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> < 0.001

Δρ<sub>max</sub> = 0.25 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.22 e Å<sup>-3</sup>

Extinction correction: *SHELXL2014* (Sheldrick,  
2015), *F<sub>c</sub>*\* = *kF<sub>c</sub>*[1 + 0.001*xF<sub>c</sub>*<sup>2</sup>λ<sup>3</sup>/sin(2θ)]<sup>-1/4</sup>

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 ( $\text{\AA}^2$ )*

|      | <i>x</i>     | <i>y</i>     | <i>z</i>    | $U_{\text{iso}}^*/U_{\text{eq}}$ | 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 (Å<sup>2</sup>)*

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$    | $U^{23}$    |
|-----|-------------|-------------|-------------|--------------|-------------|-------------|
| 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, °)*

|         |             |          |             |
|---------|-------------|----------|-------------|
| 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 <sup>i</sup>       | 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 <sup>i</sup> —C19—C18  | 112.99 (16)  |
| O1A—C10—C11 | 117.6 (3)    | C19 <sup>i</sup> —C19—H19A | 109.0        |
| N6—C10—C11  | 118.50 (12)  | C18—C19—H19A               | 109.0        |
| C16—C11—C12 | 119.33 (13)  | C19 <sup>i</sup> —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 <sup>i</sup> | -176.11 (18) |
| C5—N7—C8—N9  | 0.06 (19)    |                              |              |

Symmetry code: (i)  $-x+1, -y+1, -z$ .

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

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

| $D-H\cdots A$                      | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------------|-------|-------------|-------------|---------------|
| O2—H2A $\cdots$ N1 <sup>ii</sup>   | 0.82  | 1.92        | 2.7327 (19) | 175           |
| N6—H6 $\cdots$ O3A <sup>iii</sup>  | 0.86  | 2.09        | 2.904 (11)  | 157           |
| N7—H7 $\cdots$ O1A                 | 0.86  | 2.04        | 2.616 (16)  | 124           |
| N7—H7 $\cdots$ N9 <sup>iv</sup>    | 0.86  | 2.17        | 2.9271 (17) | 146           |
| C19—H19B $\cdots$ O3A <sup>v</sup> | 0.97  | 2.54        | 3.481 (11)  | 164           |
| C2—H2 $\cdots$ Cg3 <sup>vi</sup>   | 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)  $x, y-1, z$ .