Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Supramolecular hydrogen-bonding patterns in the N(9)—H protonated and N(7)—H tautomeric form of an N^6-benzoyladenine salt: N^6-benzoyladeninium nitrate

Ammasai Karthikeyan,[a] Nithianantham Jeeva Jasmine,[a] Packianathan Thomas Muthiah[a]* and Franc Perdih[b]

[a]School of Chemistry, Bharathidasan University, Tiruchirappalli 620024, Tamilnadu, India, and [b]Faculty of Chemistry and Chemical Technology, University of Ljubljana, Vecna pot 113, PO Box 537, SI-1000 Ljubljana, Slovenia. *Correspondence e-mail: tommtrichy@yahoo.co.in

Received 9 December 2015
Accepted 29 December 2015

Edited by J. Simpson, University of Otago, New Zealand

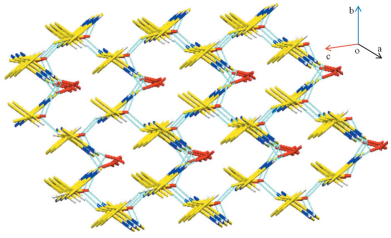
Keywords: crystal structure; N^6-benzoyl adenine; nitrate anion; hydrogen bonding; supramolecular architecture

CCDC reference: 1444600
Supporting information: this article has supporting information at journals.iucr.org/e

In the title molecular salt, $C_{12}H_{10}N_5O^+\cdot NO_3^-$, the adenine unit has an N^9-protonated N(7)—H tautomeric form with non-protonated N^1 and N^3 atoms. The dihedral angle between the adenine ring system and the phenyl ring is 51.10 (10)°. The typical intramolecular N^7—H···O hydrogen bond with an $S(7)$ graph-set motif is also present. The benzoyladeninium cations also form base pairs through N—H···O and C—H···N hydrogen bonds involving the Watson–Crick face of the adenine ring and the C and O atoms of the benzoyl ring of an adjacent cation, forming a supramolecular ribbon with $R_2^2(9)$ rings. Benzoyladeninum cations are also bridged by one of the oxygen atoms of the nitrate anion, which acts as a double acceptor, forming a pair of N—H···O hydrogen bonds to generate a second ribbon motif. These ribbons together with π–π stacking interactions between the phenyl ring and the five- and six-membered adenine rings of adjacent molecules generate a three-dimensional supramolecular architecture.

1. Chemical context

Non-covalent interactions, such as hydrogen bonding, halogen bonding and π–π interactions play major roles in molecular recognition and pharmaceutical drug design processes (Desiraju, 1989; Perumalla & Sun, 2014). N^6-substituted adenine compounds continue to attract interest due to their biological activity as they can act as plant hormones and have anti-allergenic, antibacterial, antiviral and antifungal properties (Hall, 1973; McHugh & Erxleben, 2011). N^6-substituted adenine compounds also exhibit an extensive variety of hydrogen-bonding patterns and supramolecular architectures (Raghunathan & Pattabhi, 1981; Nirmalram *et al.*, 2011; Tamilselvi & Muthiah, 2011; McHugh & Erxleben, 2011; Jennifer *et al.*, 2014). The present investigation deals with the nitrate salt of N^9-protonated benzoyladenine (I). Nitrate ions are known to play pivotal roles in hydrogen bonded supramolecular architectures, as they have three oxygen atoms to act as good hydrogen bond acceptors (Murugesan *et al.*, 1997; Cherouana *et al.*, 2003; Balasubramani *et al.*, 2005; Nirmalram *et al.*, 2011).



2. Structural commentary

The asymmetric unit of compound (I) consists of one N^6-benzoyladeninium cation and one nitrate anion, Fig. 1. In this

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

D—H···A	D—H	H···A	D···A	D—H···A
N6—H6···O1^{i}	0.86	2.33	3.135 (3)	156
N7—H7···O1	0.86	2.12	2.668 (3)	121
N7—H7···O3	0.86	1.99	2.709 (3)	140
N9—H9···O3^{ii}	0.86	1.80	2.646 (3)	169
C16—H16···N1^{iii}	0.93	2.55	3.426 (4)	157

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

salt, the N^6-benzoyladenine moiety is found in the N(7)—H tautomeric form with N9 protonated and N1, N3 non-protonated. The internal angles at N7 [C8—N7—C5 = 108.9 (2)°] and N9 [C8—N9—C4 = 107.9 (2)°] are similar as both carry hydrogen atoms (Raghunathan & Pattabhi, 1981; Raghunathan *et al.*, 1983; Nirmalram *et al.*, 2011; Tamilselvi & Muthiah, 2011; García-Terán *et al.*, 2004; Bo *et al.*, 2006). The internal angles at N1 [C6—N1—C2 = 118.9 (3)°] and N3 [C4—N3—C2 = 111.0 (3)°] agree with those reported for the neutral six-membered rings in other ademine structures (Raghunathan & Pattabhi, 1981; Karthikeyan *et al.*, 2015). An intramolecular N7—H7···O1 hydrogen bond (Table 1) is observed on the Hoogsteen face of the purine ring with the benzoyl oxygen atom, generating an $S(7)$ ring motif. A similar bond was found in the crystal structure of the neutral N^6-benzoyl adenine (Raghunathan & Pattabhi, 1981). The dihedral angle between the adenine ring system and the phenyl ring is 51.10 (10)°, and the C6—N6—C10—C11 torsion angle is −168.8 (2). The bond lengths and bond angles for the nitrate anion are in good agreement with literature values (Nirmalram *et al.*, 2011). Tables comparing dihedral and torsion angles in the title compound with those in related structures appear in the supporting information.

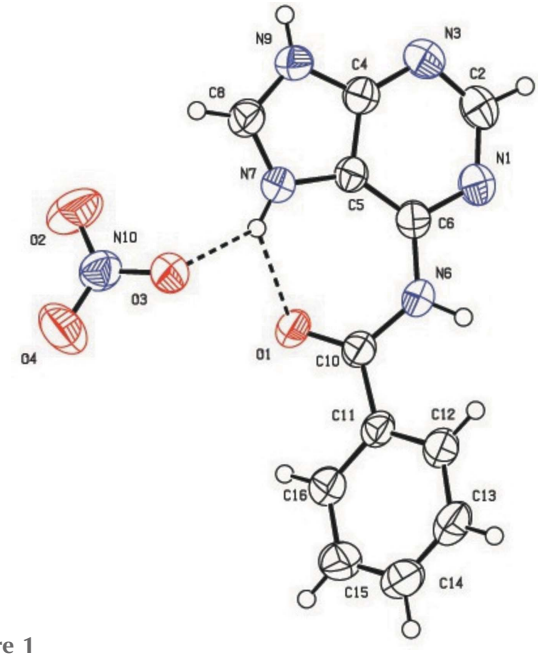
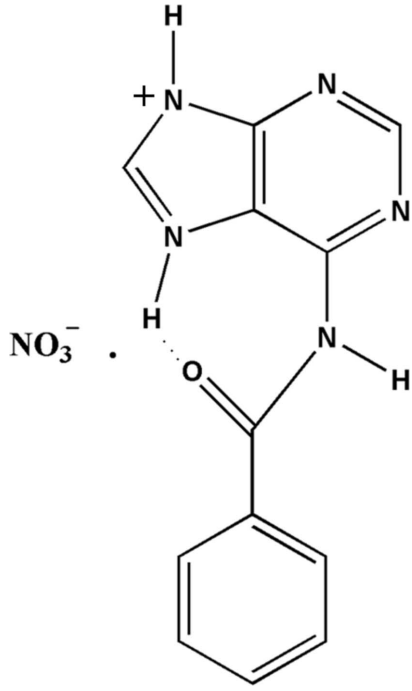


Figure 1
The asymmetric unit of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines represent hydrogen bonds.



3. Supramolecular features

In the crystal structure of (I), the benzoyladeninium cations form base pairs *via* N—H···O and C—H···N hydrogen bonds (Table 1) involving the N1 and N6 atoms on the Watson–Crick face of the adenine ring system and the C16 and O1 atoms of the benzoyl ring of an adjacent benzoyladeninium cation. These result in the formation of a supramolecular ribbon based on $R_2^2(9)$ rings, Fig. 2*a*. The benzoyladeninum cations

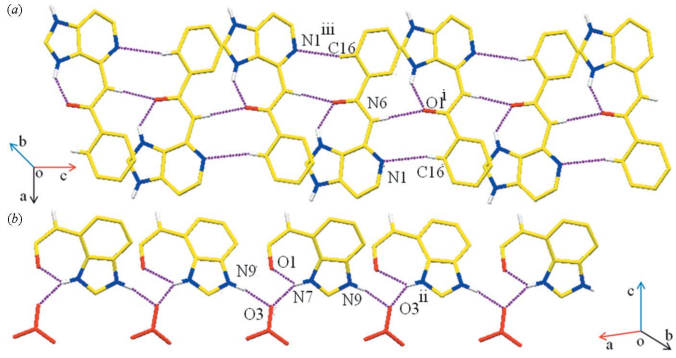


Figure 2
A view of two supramolecular ribbons of (I). (*a*) A view of adeninium–benzoyl interactions *via* N—H···O and C—H···N hydrogen bonding, forming a supramolecular ribbon. (*b*) A view of adeninum cations bridged by one of the oxygen atoms of the nitrate anion *via* N9—H9···O3 and N7—H7···O3 hydrogen bonds (purple dashed lines), generating a second type of ribbon motif. The phenyl groups and H atoms not involved in hydrogen bonding have been omitted for clarity. The symmetry codes are as given in Table 1.

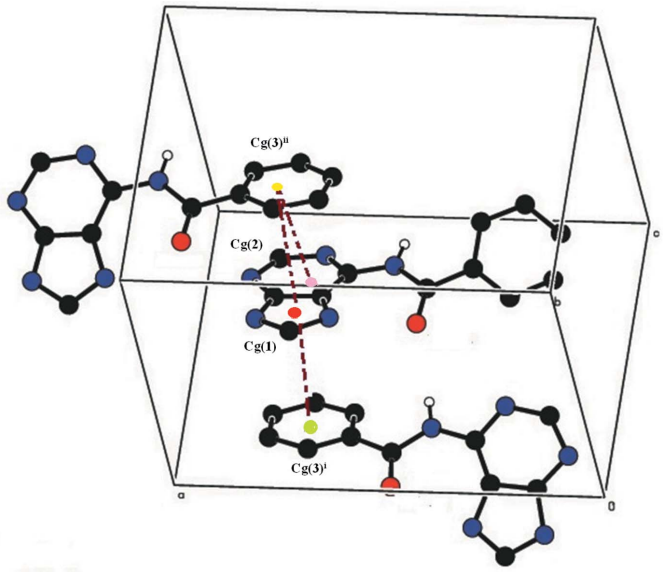


Figure 3
A view of π–π stacking interactions in (I). *Cg*1 is the centroid of the imidazole ring, *Cg*2 that of the pyrimidine ring, *Cg*3 that of the phenyl ring. Dashed lines indicate stacking interactions. Symmetry codes: (i) $1-x, -y, -\frac{1}{2}+z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, z$.

are also bridged by the O3 oxygen atoms of the nitrate anion, which acts as a bifurcated acceptor, forming N9—H9···O3 and N7—H7···O3 hydrogen bonds to generate a second ribbon motif, Fig. 2*b*. π–π stacking interactions occur between the one face of the C11–C16 phenyl ring and the C4/C5/N7/C8/N9 imidazole ring with a relatively short centroid-to-centroid separation $Cg1\cdots Cg3^{i}$ = 3.4919 (17) Å [symmetry code: (i) $1-x, -y, -\frac{1}{2}+z$]. The other face of the phenyl ring makes offset π–π contacts with both the imidazole [$Cg1\cdots Cg3^{ii}$ = 3.7213 (17) Å] and the pyrimidine rings [$Cg2\cdots Cg3^{ii}$ = 3.5362 (16) Å; symmetry code (ii) $\frac{1}{2}+x, \frac{1}{2}-y, z$], Fig. 3. *Cg*1, *Cg*2 and *Cg*3 are the centroids of the imidazole, pyrimidine and phenyl rings, respectively. Similar contacts are found in related structures (Raghunathan & Pattabhi, 1981; Karthikeyan *et al.*, 2015). These various contacts combine to generate a three-dimensional supramolecular architecture Fig. 4.

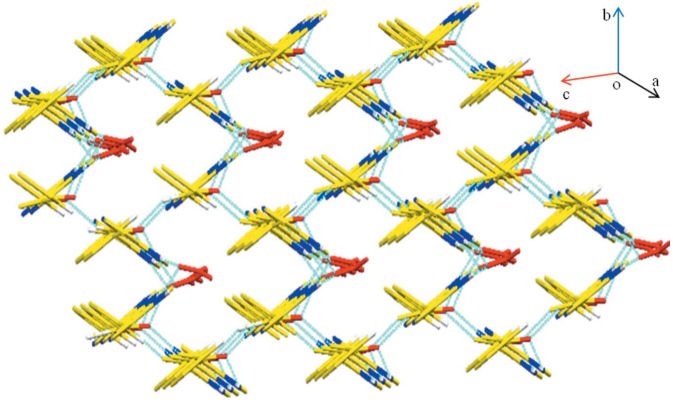


Figure 4
Overall packing in (I) viewed along the *a*-axis direction. Hydrogen bonds are drawn as light-blue dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_{10}N_5O^+\cdot NO_3^-$
M_r	302.26
Crystal system, space group	Orthorhombic, $Pna2_1$
Temperature (K)	293
a, *b*, *c* (Å)	12.7949 (10), 10.5639 (9), 9.6676 (6)
V (Å^3)	1306.71 (17)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.12
Crystal size (mm)	0.33 × 0.30 × 0.20
Data collection	
Diffractometer	Agilent SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2013)
T_{min}, T_{max}	0.791, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4891, 2559, 2080
R_{int}	0.021
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.097, 1.10
No. of reflections	2559
No. of parameters	200
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.19, −0.14

Computer programs: *CrysAlis PRO* (Agilent, 2013), *SIR97* (Altomare, 1999), *SHELXL2014/7* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008).

4. Database Survey

The crystal structures of a number of N^6-substituted adenines, adeninium salts and their metal complexes have been investigated in a variety of crystalline environments. Neutral molecules include N^6-benzyladenine (Raghunathan *et al.*, 1983), N^6-furfuryladenine (Soriano-Garcia & Parthasarathy, 1977) and N^6-benzoyladenine (Raghunathan & Pattabhi, 1981). Recently our group reported the formation of two co-crystals, N^6-benzoyladenine–3-hydroxypyridinium-2-carboxylate (1:1) and N^6-benzoyladenine–DL-tartaric acid (1:1). In these, the benzoyladenine molecule has a conformation similar to that reported for the neutral benzoyladenine crystal structure (Karthikeyan *et al.*, 2015). N^6-benzyladeninum salts with a wide variety of counter-anions have also been reported (Umadevi *et al.*, 2001; Xia *et al.*, 2010; Nirmalram *et al.*, 2011; Tamilselvi & Muthiah, 2011; McHugh & Erxleben, 2011; Stanley *et al.*, 2003). A variety of metal complexes of neutral N^6-benzyl/furfuryladenines have been reported (Jennifer *et al.*, 2014), while structures of copper complexes of N^6-furfuryladeninium (Umadevi *et al.*, 2002) and N^6-benzyladeninium (Balasubramanian *et al.*, 1996) are also known.

5. Synthesis and crystallization

To a hot methanol solution of N^6-benzolyadenine (60 mg), a few drops of nitric acid were added. The resulting solution was

warmed over a water bath for half an hour and then kept at room temperature for crystallization. After a week colourless prismatic crystals of (I) were obtained.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. 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 and N—H = 0.86 Å, and with U_{iso}(H) = 1.2U_{eq}(C, N).

Acknowledgements

AK and NJJ thank the UGC–SAP and UGC–BSR India for the award of an RFSMS. PTM is thankful to the UGC, New Delhi, for a UGC–BSR one-time grant to Faculty. FP thanks the Slovenian Research Agency for financial support (P1–0230–0175), as well as the EN–FIST Centre of Excellence, Trg Osvobodilne fronte 13, 1000 Ljubljana, Slovenia, for use of the SuperNova diffractometer.

References

Agilent (2013). *CrysAlis PRO*. Agilent Technologies UK Ltd, Yarnton, England.
Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Balasubramani, K., Muthiah, P. T., Rychlewska, U. & Plutecka, A. (2005). *Acta Cryst.* C**61**, o586–o588.
Balasubramanian, T., Muthiah, P. T., Ananthasaravanan, & Mazumdar, S. K. (1996). *J. Inorg. Biochem.* **63**, 175–181.
Bo, Y., Cheng, K., Bi, S. & Zhang, S.-S. (2006). *Acta Cryst.* E**62**, o4174–o4175.
Cherouana, A., Bouchouit, K., Bendjeddou, L. & Benali-Cherif, N. (2003). *Acta Cryst.* E**59**, o983–o985.
Desiraju, G. R. (1989). *Crystal engineering: the design of organic solids*. Amsterdam: Elsevier.
García-Terán, J. P., Castillo, O., Luque, A., García-Couceiro, U., Román, P. & Lloret, F. (2004). *Inorg. Chem.* **43**, 5761–5770.
Hall, R. H. (1973). *Annu. Rev. Plant Physiol.* **24**, 415–444.
Jennifer, S. J., Thomas Muthiah, P. & Tamilselvi, D. (2014). *Chem. Cent. J.* **8**, 58.
Karthikeyan, A., Swinton Darious, R., Thomas Muthiah, P. & Perdih, F. (2015). *Acta Cryst.* C**71**, 985–990.
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.
McHugh, C. & Erxleben, A. (2011). *Cryst. Growth Des.* **11**, 5096–5104.
Murugesan, S. & Muthiah, P. T. (1997). *Acta Cryst.* C**53**, 763–764.
Nirmalram, J. S., Tamilselvi, D. & Muthiah, P. T. (2011). *J. Chem. Crystallogr.* **41**, 864–867.
Perumalla, S. R. & Sun, C. C. (2014). *J. Pharm. Sci.* **103**, 1126–1132.
Raghunathan, S. & Pattabhi, V. (1981). *Acta Cryst.* B**37**, 1670–1673.
Raghunathan, S., Sinha, B. K., Pattabhi, V. & Gabe, E. J. (1983). *Acta Cryst.* C**39**, 1545–1547.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Soriano-Garcia, M. & Parthasarathy, R. (1977). *Acta Cryst.* B**33**, 2674–2677.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Stanley, N., Muthiah, P. T. & Geib, S. J. (2003). *Acta Cryst.* C**59**, o27–o29.
Tamilselvi, D. & Muthiah, P. T. (2011). *Acta Cryst.* C**67**, o192–o194.
Umadevi, B., Stanley, N., Muthiah, P. T., Bocelli, G. & Cantoni, A. (2001). *Acta Cryst.* E**57**, o881–o883.
Umadevi, B., Stanley, N., Muthiah, P. T. & Varghese, B. (2002). *Indian J. Chem.* **A41**, 737–740.
Xia, M., Ma, K. & Zhu, Y. (2010). *J. Chem. Crystallogr.* **40**, 634–638.

supporting information

Acta Cryst. (2016). E**72**, 140-143 [doi:10.1107/S2056989015024871]

Supramolecular hydrogen-bonding patterns in the N(9)—H protonated and N(7)—H tautomeric form of an N^6-benzoyladenine salt: N^6-benzoyladeninium nitrate

Ammasai Karthikeyan, Nithianantham Jeeva Jasmine, Packianathan Thomas Muthiah and Franc Perdih

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: *SIR97* (Altomare, 1999); program(s) used to refine structure: *SHELXL2014*/7 (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009), *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *PLATON* (Spek, 2009).

N^6-benzoyladeninium nitrate

Crystal data

$C_{12}H_{10}N_5O^+\cdot NO_3^-$
M_r = 302.26
Orthorhombic, $Pna2_1$
a = 12.7949 (10) Å
b = 10.5639 (9) Å
c = 9.6676 (6) Å
V = 1306.71 (17) Å^3
Z = 4
$F(000)$ = 624
D_x = 1.536 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1553 reflections
θ = 3.7–27.6°
μ = 0.12 mm^{-1}
T = 293 K
Prism, colorless
0.33 × 0.30 × 0.20 mm

Data collection

Agilent SuperNova, Dual, Cu at zero, Atlas diffractometer
Detector resolution: 10.4933 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013)
T_{min} = 0.791, T_{max} = 1.000
4891 measured reflections
2559 independent reflections
2080 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 27.5°, θ_{min} = 2.9°
h = −16→11
k = −13→9
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.097
S = 1.10
2559 reflections
200 parameters
1 restraint
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

Extinction correction: *SHELXL2014*/7 (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0092 (16)

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.7324 (2)	0.0197 (2)	0.8356 (3)	0.0543 (7)
N3	0.8848 (2)	0.0766 (2)	0.7035 (3)	0.0546 (7)
N6	0.56197 (18)	0.0580 (2)	0.7771 (2)	0.0458 (6)
H6	0.5487	0.0479	0.8637	0.055*
N7	0.67166 (18)	0.1685 (2)	0.5004 (2)	0.0437 (6)
H7	0.6070	0.1798	0.4795	0.052*
N9	0.84001 (19)	0.1733 (2)	0.4852 (2)	0.0467 (6)
H9	0.9016	0.1874	0.4532	0.056*
O1	0.48787 (16)	0.0648 (2)	0.5649 (2)	0.0540 (6)
C2	0.8360 (3)	0.0298 (3)	0.8128 (4)	0.0591 (9)
H2	0.8789	0.0000	0.8833	0.071*
C4	0.8168 (2)	0.1171 (2)	0.6093 (3)	0.0425 (7)
C5	0.7080 (2)	0.1128 (2)	0.6197 (3)	0.0379 (6)
C6	0.6665 (2)	0.0629 (2)	0.7404 (3)	0.0420 (7)
C8	0.7516 (2)	0.2016 (3)	0.4239 (3)	0.0478 (7)
H8	0.7463	0.2400	0.3376	0.057*
C10	0.4770 (2)	0.0675 (2)	0.6908 (3)	0.0405 (6)
C11	0.3735 (2)	0.0836 (2)	0.7561 (3)	0.0406 (6)
C12	0.3614 (2)	0.1411 (3)	0.8840 (3)	0.0471 (7)
H12	0.4197	0.1645	0.9354	0.056*
C13	0.2615 (3)	0.1635 (3)	0.9351 (3)	0.0559 (8)
H13	0.2532	0.2035	1.0201	0.067*
C14	0.1755 (3)	0.1272 (3)	0.8610 (4)	0.0580 (8)
H14	0.1090	0.1420	0.8963	0.070*
C15	0.1868 (3)	0.0689 (3)	0.7344 (4)	0.0581 (9)
H15	0.1280	0.0437	0.6848	0.070*
C16	0.2852 (2)	0.0480 (3)	0.6814 (3)	0.0483 (7)
H16	0.2928	0.0100	0.5952	0.058*
N10	0.5040 (2)	0.2616 (3)	0.2263 (3)	0.0563 (7)
O2	0.5789 (2)	0.2331 (3)	0.1545 (3)	0.0904 (9)
O3	0.51791 (16)	0.2830 (2)	0.3540 (2)	0.0660 (7)
O4	0.4156 (2)	0.2712 (3)	0.1814 (3)	0.0993 (10)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0528 (16)	0.0628 (16)	0.0473 (14)	0.0062 (12)	−0.0050 (13)	0.0127 (14)
N3	0.0460 (14)	0.0608 (14)	0.0571 (17)	0.0070 (13)	−0.0043 (15)	0.0027 (15)
N6	0.0458 (13)	0.0589 (14)	0.0326 (12)	−0.0001 (11)	0.0032 (12)	0.0047 (11)
N7	0.0400 (13)	0.0536 (13)	0.0375 (13)	−0.0021 (11)	0.0002 (11)	0.0048 (11)
N9	0.0399 (13)	0.0549 (13)	0.0452 (14)	−0.0060 (11)	0.0022 (12)	−0.0012 (12)
O1	0.0503 (12)	0.0780 (15)	0.0338 (11)	−0.0144 (11)	0.0053 (10)	−0.0019 (10)
C2	0.055 (2)	0.068 (2)	0.054 (2)	0.0108 (16)	−0.0108 (17)	0.0123 (17)
C4	0.0442 (15)	0.0420 (13)	0.0415 (16)	0.0011 (13)	0.0011 (14)	−0.0050 (14)
C5	0.0403 (14)	0.0390 (12)	0.0344 (13)	0.0004 (12)	0.0004 (13)	−0.0039 (12)
C6	0.0448 (14)	0.0439 (14)	0.0375 (15)	0.0027 (12)	−0.0021 (15)	−0.0002 (13)
C8	0.0484 (17)	0.0536 (15)	0.0412 (16)	−0.0086 (14)	0.0019 (14)	0.0024 (14)
C10	0.0430 (15)	0.0427 (14)	0.0357 (15)	−0.0027 (12)	0.0024 (13)	0.0008 (13)
C11	0.0443 (15)	0.0428 (13)	0.0347 (13)	−0.0008 (12)	0.0049 (13)	0.0066 (12)
C12	0.0512 (16)	0.0514 (15)	0.0386 (15)	0.0021 (14)	0.0031 (15)	0.0021 (14)
C13	0.066 (2)	0.0601 (18)	0.0417 (17)	0.0105 (17)	0.0136 (16)	0.0033 (16)
C14	0.0522 (19)	0.0625 (18)	0.059 (2)	0.0077 (16)	0.0137 (18)	0.0131 (18)
C15	0.0493 (18)	0.0646 (18)	0.060 (2)	−0.0075 (16)	0.0022 (18)	0.0105 (18)
C16	0.0494 (18)	0.0532 (15)	0.0425 (15)	−0.0033 (14)	0.0018 (16)	0.0036 (15)
N10	0.0528 (17)	0.0612 (15)	0.0549 (16)	0.0087 (14)	0.0073 (15)	0.0001 (13)
O2	0.0774 (17)	0.1083 (19)	0.086 (2)	0.0132 (16)	0.0372 (16)	−0.0060 (17)
O3	0.0484 (13)	0.1011 (18)	0.0485 (13)	0.0120 (12)	−0.0007 (11)	0.0072 (14)
O4	0.0652 (16)	0.159 (3)	0.0738 (18)	0.0326 (19)	−0.0219 (15)	−0.0447 (19)

Geometric parameters (Å, º)

N1—C6	1.330 (4)	C8—H8	0.9300
N1—C2	1.347 (4)	C10—C11	1.477 (4)
N3—C2	1.323 (4)	C11—C12	1.386 (4)
N3—C4	1.330 (4)	C11—C16	1.393 (4)
N6—C10	1.374 (4)	C12—C13	1.390 (4)
N6—C6	1.384 (4)	C12—H12	0.9300
N6—H6	0.8600	C13—C14	1.367 (5)
N7—C8	1.309 (3)	C13—H13	0.9300
N7—C5	1.376 (3)	C14—C15	1.378 (5)
N7—H7	0.8600	C14—H14	0.9300
N9—C8	1.312 (4)	C15—C16	1.378 (4)
N9—C4	1.371 (4)	C15—H15	0.9300
N9—H9	0.8600	C16—H16	0.9300
O1—C10	1.226 (3)	N10—O4	1.216 (3)
C2—H2	0.9300	N10—O2	1.222 (3)
C4—C5	1.397 (4)	N10—O3	1.268 (4)
C5—C6	1.386 (4)		
C6—N1—C2	118.9 (3)	N9—C8—H8	124.5
C2—N3—C4	111.0 (3)	O1—C10—N6	120.8 (3)

C10—N6—C6	127.3 (2)	O1—C10—C11	121.9 (3)
C10—N6—H6	116.4	N6—C10—C11	117.3 (2)
C6—N6—H6	116.4	C12—C11—C16	119.3 (3)
C8—N7—C5	108.9 (2)	C12—C11—C10	122.2 (3)
C8—N7—H7	125.6	C16—C11—C10	118.3 (3)
C5—N7—H7	125.6	C11—C12—C13	119.6 (3)
C8—N9—C4	107.9 (3)	C11—C12—H12	120.2
C8—N9—H9	126.0	C13—C12—H12	120.2
C4—N9—H9	126.0	C14—C13—C12	120.4 (3)
N3—C2—N1	128.6 (3)	C14—C13—H13	119.8
N3—C2—H2	115.7	C12—C13—H13	119.8
N1—C2—H2	115.7	C13—C14—C15	120.4 (3)
N3—C4—N9	126.7 (3)	C13—C14—H14	119.8
N3—C4—C5	126.3 (3)	C15—C14—H14	119.8
N9—C4—C5	107.0 (2)	C16—C15—C14	119.8 (3)
N7—C5—C6	137.6 (3)	C16—C15—H15	120.1
N7—C5—C4	105.2 (2)	C14—C15—H15	120.1
C6—C5—C4	117.1 (3)	C15—C16—C11	120.4 (3)
N1—C6—N6	115.0 (2)	C15—C16—H16	119.8
N1—C6—C5	118.0 (2)	C11—C16—H16	119.8
N6—C6—C5	126.9 (3)	O4—N10—O2	123.2 (3)
N7—C8—N9	110.9 (3)	O4—N10—O3	117.6 (3)
N7—C8—H8	124.5	O2—N10—O3	119.1 (3)

C4—N3—C2—N1	0.3 (5)	N7—C5—C6—N6	−1.3 (5)
C6—N1—C2—N3	−1.4 (5)	C4—C5—C6—N6	174.9 (3)
C2—N3—C4—N9	178.5 (3)	C5—N7—C8—N9	−0.9 (3)
C2—N3—C4—C5	−0.1 (4)	C4—N9—C8—N7	0.5 (3)
C8—N9—C4—N3	−178.7 (3)	C6—N6—C10—O1	9.9 (4)
C8—N9—C4—C5	0.1 (3)	C6—N6—C10—C11	−168.8 (2)
C8—N7—C5—C6	177.4 (3)	O1—C10—C11—C12	−150.8 (3)
C8—N7—C5—C4	1.0 (3)	N6—C10—C11—C12	27.9 (4)
N3—C4—C5—N7	178.2 (3)	O1—C10—C11—C16	24.4 (4)
N9—C4—C5—N7	−0.6 (3)	N6—C10—C11—C16	−156.9 (2)
N3—C4—C5—C6	0.9 (4)	C16—C11—C12—C13	−0.7 (4)
N9—C4—C5—C6	−178.0 (2)	C10—C11—C12—C13	174.5 (3)
C2—N1—C6—N6	−175.0 (3)	C11—C12—C13—C14	1.2 (4)
C2—N1—C6—C5	2.1 (4)	C12—C13—C14—C15	−0.5 (5)
C10—N6—C6—N1	−163.5 (2)	C13—C14—C15—C16	−0.6 (4)
C10—N6—C6—C5	19.7 (4)	C14—C15—C16—C11	1.1 (4)
N7—C5—C6—N1	−178.0 (3)	C12—C11—C16—C15	−0.4 (4)
C4—C5—C6—N1	−1.9 (4)	C10—C11—C16—C15	−175.8 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6···O1^{i}	0.86	2.33	3.135 (3)	156
N7—H7···O1	0.86	2.12	2.668 (3)	121

N7—H7···O3	0.86	1.99	2.709 (3)	140
N9—H9···O3^{ii}	0.86	1.80	2.646 (3)	169
C16—H16···N1^{iii}	0.93	2.55	3.426 (4)	157

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