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Hydrogen-bonding patterns in 5-fluorocytosine–melamine co-crystal (4/1)

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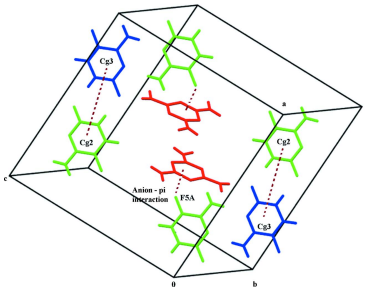
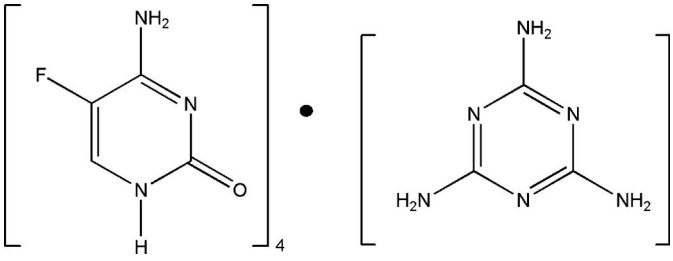
The asymmetric unit of the title compound, $4C_4H_4FN_3O\cdot C_3H_6N_6$, comprises of two independent 5-fluorocytosine (5FC) molecules (*A* and *B*) and one half-molecule of melamine (*M*). The other half of the melamine molecule is generated by a twofold axis. 5FC molecules *A* and *B* are linked through two different homosynthons [$R_2^2(8)$ ring motif]; one is formed *via* a pair of N—H···O hydrogen bonds and the second *via* a pair of N—H···N hydrogen bonds. In addition to this pairing, the O atoms of 5FC molecules *A* and *B* interact with the N2 amino group on both sides of the melamine molecule, forming a *DDAA* array of quadruple hydrogen bonds and generating a supramolecular pattern. The 5FC (molecules *A* and *B*) and two melamine molecules interact *via* N—H···O, N—H···N and N—H···O, N—H···N, C—H···F hydrogen bonds forming $R_6^6(24)$ and $R_4^4(15)$ ring motifs. The crystal structure is further strengthened by C—H···F, C—F···π and π–π stacking interactions.

1. Chemical context

Pyrimidine derivatives are used in the treatment of antiviral, antifungal, antitumor and cardiovascular diseases. 5-Fluorocytosine (5FC), a synthetic antimycotic compound, first synthesized in 1957 and widely used as an antitumor agent as a cytosine derivative (Tassel & Madoff, 1968; Benson & Nahata, 1988; Bennet, 1977; Polak & Scholer, 1980). It is active against fungal infection and was released in the year 1968 (Vermes *et al.*, 2000). It becomes active by deamination of 5FC into 5-fluorouracil by the enzyme cytosine deaminase (CD) and inhibits RNA and DNA synthesis (Larsen *et al.*, 2003; Mullen *et al.*, 1994; Morschhäuser, 2003). Melamine is a triazine derivative. It shows antitumor activity as well as biological activities such as antiangiogenesis and antimicrobial effects. Triazine derivatives are useful synthons in supramolecular chemistry. In particular, aminotriazines have been used for the formation of supramolecular architectures using hydrogen bonds (Russell *et al.*, 1998; MacDonald & Whitesides, 1994; Whitesides *et al.*, 1991). The organic and inorganic salts develop well-defined non-covalent molecular recognition *via* multiple hydrogen bonds by self assembly of components which contain a complementary array of hydrogen-bonding sites (Desiraju, 1989). The present work is focused on the supramolecular hydrogen-bonding patterns exhibited by the co-crystal of 5-fluorocytosine with melamine.





2. Structural commentary

The asymmetric unit comprises two independent 5-fluorocytosine (5FC) molecules (*A* and *B*) and half a molecule of melamine (*M*). The twofold axis of melamine coincides with the crystallographic twofold axis. An *ORTEP* view of the crystal structure is shown in Fig. 1. The values for the C—F bond distance in the two molecules [1.3491 (18) in 5FC *A* and 1.3492 (18) Å in 5FC *B* and the corresponding internal angles at the carbon-carrying fluorine atom [C2*A*—N3*A*—C4*A* = 119.96 (13) in 5FC *A* and C2*B*—N3*B*—C4*B* = 119.92 (13)° in 5FC *B*] agree with those reported in the literature (Louis *et al.*, 1982).

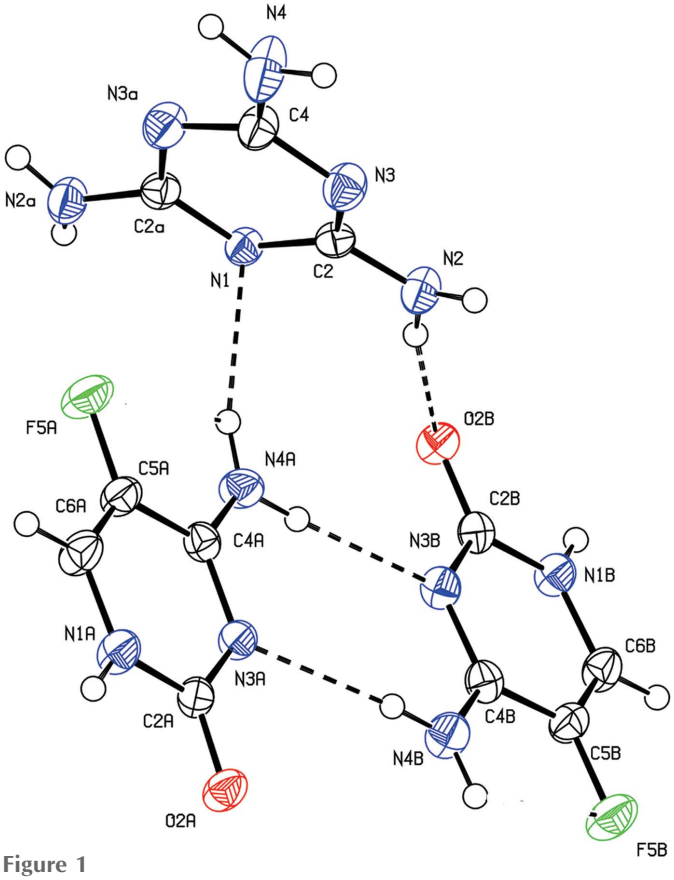


Figure 1
The asymmetric unit of the title compound, showing 30% probability displacement ellipsoids. Dashed lines indicate hydrogen bonds. Atoms with the suffix a are generated by the symmetry operation 1 − *x*, *y*, {\script{1\over 2}} − *z*.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4*A*—H4*A*1···F5*A*	0.86 (2)	2.47 (2)	2.7560 (18)	100.0 (18)
N4*A*—H4*A*1···N1	0.86 (2)	2.23 (2)	3.0664 (18)	164 (2)
N1*A*—H1*A*···O2*B*^{ii}	0.88	1.90	2.773 (2)	173
N1*B*—H1*B*···O2*A*^{iii}	0.88	1.88	2.7545 (19)	175
N4*A*—H4*A*2···N3*B*	0.91 (2)	2.10 (2)	2.992 (2)	169 (2)
N2—H2*A*···O2*B*	0.89 (2)	2.10 (2)	2.9689 (19)	167.6 (18)
N2—H2*B*···O2*A*^{iv}	0.84 (2)	2.15 (2)	2.8949 (19)	149 (2)
N4*B*—H4*B*1···N3*A*	0.88 (2)	2.20 (2)	3.060 (2)	169 (2)
N4*B*—H4*B*2···F5*B*	0.86 (2)	2.42 (2)	2.7459 (19)	103 (2)
N4*B*—H4*B*2···N3^{iv}	0.86 (2)	2.53 (2)	3.360 (2)	162 (2)
N4—H4*A*···O2*B*^{v}	0.89 (2)	2.09 (2)	2.9600 (15)	165 (2)
C6*B*—H6*B*···F5*A*^{vi}	0.95	2.43	3.2444 (19)	143

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

3. Supramolecular features

Two different homosynthons are assembled *via* a pair of N—H···O and N—H···N hydrogen bonds (Table 1) to render a robust $R_2^2(8)$ ring motif. The first type of homosynthon is formed by the interaction of the protonated N1 and O atoms of 5FC molecules *A* and *B* through N—H···O hydrogen bonds. Another type of homosynthon is formed *via* the N4-amino and N3-pyrimidine ring nitrogen atoms of the 5FC *A* and *B* molecules through a pair of N—H···N hydrogen bonds (da Silva *et al.*, 2013; Tutughamiarso *et al.*, 2012). The melamine molecule and 5FC (molecules *A* and *B*) are involved in the generation of a quadruple hydrogen-bonded *DDAA* array

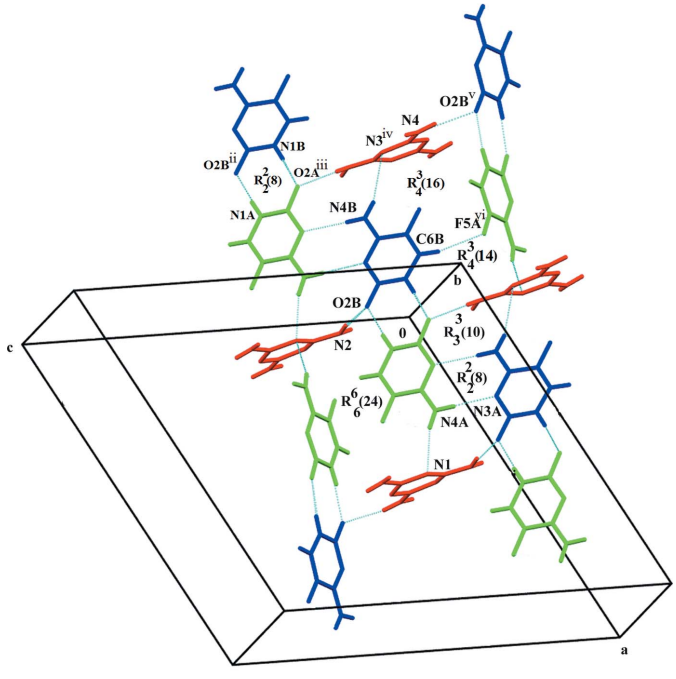


Figure 2
A view of the supramolecular pattern involving two synthons formed by N—H···O hydrogen bonds. 5FC *A* molecules are shown in green, 5FC *B* molecules in blue and melamine in red. Blue dashed lines indicate hydrogen bonds. Symmetry codes are given in Table 1.

having a fused-ring sequence of $R_3^3(10)$, $R_2^2(8)$ and $R_3^3(10)$. The $R_3^3(10)$ motif is formed on both sides *via* N—H···O and N—H···N hydrogen bonds. These quadruple arrays are further linked by three large ring motifs: $R_6^6(24)$, $R_4^3(16)$ and $R_4^3(14)$. The $R_6^6(24)$ ring motifs are formed by the interaction of two 5FC *A* molecules, two 5FC *B* molecules and two melamine molecules through several N—H···O and N—H···N hydrogen bonds, generating a hexameric supermolecule. The $R_4^3(16)$ ring motif links the one 5FC *A* molecule, two 5FC *B* molecules and one melamine molecule through N—H···O, N—H···N and C—H···F hydrogen bonds, generating a tetrameric supermolecule. Similarly, the $R_4^3(14)$ ring motifs are formed by the interaction of two 5FC *A* molecules, one 5FC *B* molecule and one melamine molecule through N—H···O, N—H···N and C—H···F hydrogen bonds, generating another tetrameric supermolecule. The association of these $R_2^2(8)$, *DDAA* array and $R_6^6(24)$, $R_4^3(16)$ and $R_4^3(14)$ motifs leads to the formation of supramolecular patterns (Fig. 2). The crystal structure is also stabilized by weak C—H···F hydrogen bonds and π–π stacking interactions between 5FC *A* and *B* molecules with an interplanar distance of 3.475 (6) Å, centroid-to-centroid distance of 3.6875 (11) Å, and slip angle of 19.52°. The crystal structure is further strengthened by a C—F···π interaction [3.4541 (14) Å] between 5-fluorocytosinium molecule *A* and the melamine molecule (Fig. 3).

In this co-crystal, 5FC molecules *A* and *B* form two types of homosynthons (two types of base pairing) while the melamine molecule interacts with them *via* N—H···O and N—H···N hydrogen bonds, generating the supramolecular architecture.

4. Database survey

The crystal structure of 5-fluorocytosine monohydrate (Louis *et al.*, 1982; Portalone & Colapietro, 2006; Portalone, 2011), polymorphs (Hulme & Tocher, 2006; Tutughamiarso *et al.*, 2009), salts (Perumalla *et al.*, 2013*a*,*b*) and co-crystals (Tutughamiarso *et al.*, 2012; Da Silva *et al.*, 2013) have been reported in the literature. From our laboratory, 5-fluorocytosinium salicylate (Prabakaran *et al.*, 2001) and 5-fluorocytosinium 3-hydroxypicolinate (Karthikeyan *et al.*, 2014) have been reported. Various salts, co-crystals and metal complexes of melamine have also been reported (Janczak & Perpétuo, 2001*a*,*b*, 2002, 2004; Perpétuo *et al.*, 2005; Zerkowski & Whitesides, 1994; Wang *et al.*, 2007).

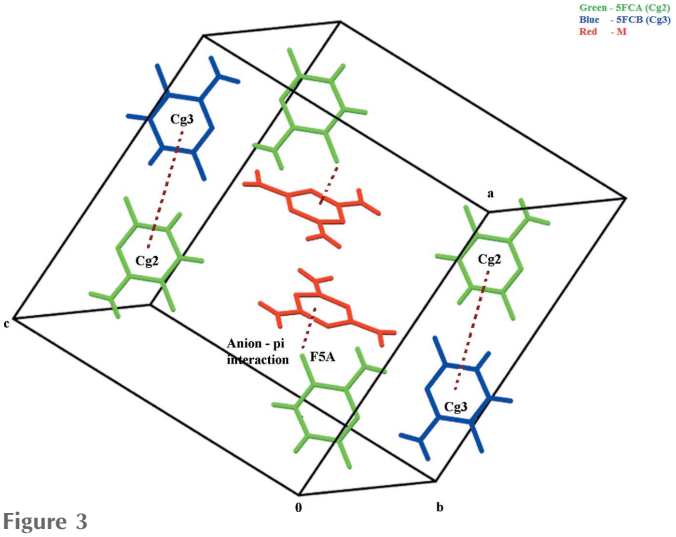


Figure 3
A view of C—F···π and aromatic π–π stacking interactions (dashed lines) between 5FC molecules *A* and *B* and melamine.

Table 2
Experimental details.

Crystal data	
Chemical formula	$4C_4H_4FN_3O{\cdot}C_3H_6N_6$
M_r	642.55
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	200
a, *b*, *c* (Å)	18.343 (4), 7.9591 (16), 19.680 (4)
β (°)	114.65 (3)
V (Å^3)	2611.3 (11)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.14
Crystal size (mm)	0.20 × 0.20 × 0.20
Data collection	
Diffractometer	Rigaku AFC–8S
Absorption correction	Multi-scan (*CrystalClear*; Rigaku/MSC, 2008)
T_{min}, T_{max}	0.972, 0.972
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10071, 2564, 2362
R_{int}	0.019
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.045, 0.123, 1.07
No. of reflections	2564
No. of parameters	233
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.44, −0.34

Computer programs: *CrystalClear* (Rigaku/MSC, 2008), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *PLATON* (Spek, 2009), *Mercury* (Macrae *et al.*, 2008), *POV-RAY* (Cason, 2004) and *publCIF* (Westrip, 2010).

5. Synthesis and crystallization

Hot aqueous solutions of 5-fluorocytosine (32 mg) and melamine (31 mg) were mixed in a 1:1 molar ratio. The resulting solution was warmed to 353 K using a water bath for half an hour and kept at room temperature for crystallization. After one week, colourless crystals were obtained.

6. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydrogen atoms of amino (N2, N4, N4*A*, N4*B*) groups were located in a difference Fourier map and refined freely. The other hydrogen atoms were positioned geometrically (C—H = 0.95, N—H = 0.88 Å) and were refined using a riding model with U_{iso}(H) = 1.2U_{eq}(parent atom).

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References

Bennet, J. E. (1977). *Ann. Intern. Med.* **86**, 319–21.
Benson, J. M. & Nahata, M. C. (1988). *Clin. Pharm.* **7**, 424–438.
Cason, C. J. (2004). *POV-RAY* for Windows. Persistence of Vision, Raytracer Pvt Ltd, Victoria, Australia. URL: *http://www.pov-ray.org*.
Desiraju, G. R. (1989). *Crystal Engineering. The Design of Organic Solids*. Amsterdam: Elsevier.
Hulme, A. T. & Tocher, D. A. (2006). *Cryst. Growth Des.* **6**, 481–487.
Janczak, J. & Perpétuo, G. J. (2001*a*). *Acta Cryst.* C**57**, 1431–1433.
Janczak, J. & Perpétuo, G. J. (2001*b*). *Acta Cryst.* C**57**, 1120–1122.
Janczak, J. & Perpétuo, G. J. (2002). *Acta Cryst.* C**58**, o339–o341.
Janczak, J. & Perpétuo, G. J. (2004). *Acta Cryst.* C**60**, o211–o214.
Karthikeyan, A., Thomas Muthiah, P. & Perdih, F. (2014). *Acta Cryst.* E**70**, 328–330.
Larsen, R. A., Kauffman, C. A., Pappas, P. G., Sobel, J. D. & Dismukes, W. E. (2003). In *Essentials of Clinical Mycology*, 2nd ed., pp. 57–60. Oxford University Press. UK.
Louis, T., Low, J. N. & Tollin, P. (1982). *Cryst. Struct. Commun.* **11**, 1059–1064.
MacDonald, J. C. & Whitesides, G. M. (1994). *Chem. Rev.* **94**, 2383–2420.
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.
Morschhäuser, J. (2003). *Pharm. Unserer Zeit*, **32**, 124–128.
Mullen, C. A., Coale, M. M., Lowe, R. & Blaese, R. M. (1994). *Cancer Res.* **54**, 1503–1506.
Perpétuo, G. J., Ribeiro, M. A. & Janczak, J. (2005). *Acta Cryst.* E**61**, o1818–o1820.
Perumalla, S. R., Pedireddi, V. R. & Sun, C. C. (2013*a*). *Cryst. Growth Des.* **13**, 429–432.
Perumalla, S. R., Pedireddi, V. R. & Sun, C. C. (2013*b*). *Mol. Pharm.* **10**, 2462–2466.
Polak, A. & Scholer, H. J. (1980). *Rev. Inst. Pasteur Lyon.* **13**, 233–244.
Portalone, G. (2011). *Chem. Cent. J.* **5**, 51.
Portalone, G. & Colapietro, M. (2006). *Acta Cryst.* E**62**, o1049–o1051.
Prabakaran, P., Murugesan, S., Muthiah, P. T., Bocelli, G. & Righi, L. (2001). *Acta Cryst.* E**57**, o933–o936.
Rigaku/MSC (2008). *CrystalClear*. Rigaku Americas Corporation, The Woodlands, Texas, USA.
Russell, K. C., Lehn, J. M., Kyritsakas, N., DeCian, A. & Fischer, J. (1998). *New J. Chem.* **22**, 123–128.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Silva, C. C. P. da, de Oliveira, R., Tenorio, J. C., Honorato, S., Ayala, A. P. & Ellena, J. (2013). *Cryst. Growth Des.* **13**, 4315–4322.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Tassel, D. & Madoff, A. (1968). *J. Am. Med. Assoc.* **206**, 830–832.
Tutughamiarso, M., Bolte, M. & Egert, E. (2009). *Acta Cryst.* C**65**, o574–o578.
Tutughamiarso, M., Wagner, G. & Egert, E. (2012). *Acta Cryst.* B**68**, 431–443.
Vermes, A., Guchelaar, H. J. & Dankert, J. (2000). *J. Antimicrob. Chemother.* **46**, 171–179.
Wang, G., Wu, W. & Zhuang, L. (2007). *Acta Cryst.* E**63**, m2552–m2553.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Whitesides, G. M., Mathias, J. P. & Seto, C. T. (1991). *Science*, **254**, 1312–1319.
Zerkowski, J. A. & Whitesides, G. M. (1994). *J. Am. Chem. Soc.* **116**, 4298–4304.

supporting information

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Computing details

Data collection: *CrystalClear* (Rigaku/MSC, 2008); cell refinement: *CrystalClear* (Rigaku/MSC, 2008); data reduction: *CrystalClear* (Rigaku/MSC, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009), *Mercury* (Macrae *et al.*, 2008) and *POV-RAY* (Cason, 2004); software used to prepare material for publication: *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

4-Amino-5-fluoro-1,2-dihydropyrimidin-2-one–1,3,5-triazine-2,4,6-triamine (4/1)

Crystal data

$4(C_4H_4FN_3O)\cdot C_3H_6N_6$
M_r = 642.55
Monoclinic, $C2/c$
Hall symbol: -C 2yc
a = 18.343 (4) Å
b = 7.9591 (16) Å
c = 19.680 (4) Å
β = 114.65 (3)°
V = 2611.3 (11) Å^3
Z = 4
$F(000)$ = 1320
D_x = 1.634 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2564 reflections
θ = 2.4–26.0°
μ = 0.14 mm^{-1}
T = 200 K
Prism, colorless
0.20 × 0.20 × 0.20 mm

Data collection

Rigaku AFC–8S diffractometer
Radiation source: fine focus sealed tube
Graphite monochromator
Detector resolution: 14.6199 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2008)
T_{min} = 0.972, T_{max} = 0.972
10071 measured reflections
2564 independent reflections
2362 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 26.0°, θ_{min} = 2.4°
h = −22→18
k = −9→9
l = −24→24

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.123
S = 1.07
2564 reflections
233 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0741P)^2 + 1.8751P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.50000	0.1866 (2)	0.25000	0.0244 (5)
N2	0.48606 (8)	0.18336 (19)	0.12847 (8)	0.0326 (4)
N3	0.48592 (8)	−0.07579 (17)	0.18444 (7)	0.0342 (4)
N4	0.50000	−0.3280 (3)	0.25000	0.0501 (8)
C2	0.49100 (8)	0.09524 (18)	0.18883 (7)	0.0248 (4)
C4	0.50000	−0.1589 (3)	0.25000	0.0300 (6)
F5A	0.32327 (5)	0.12206 (14)	0.26116 (5)	0.0420 (3)
O2A	0.06416 (6)	0.34719 (15)	0.03132 (6)	0.0326 (3)
N1A	0.11896 (8)	0.17904 (17)	0.13300 (7)	0.0315 (4)
N3A	0.19980 (7)	0.34775 (15)	0.09362 (7)	0.0252 (3)
N4A	0.33640 (8)	0.35220 (17)	0.16222 (8)	0.0299 (4)
C2A	0.12590 (8)	0.29396 (19)	0.08380 (8)	0.0253 (4)
C4A	0.26467 (8)	0.29295 (18)	0.15183 (8)	0.0243 (4)
C5A	0.25656 (9)	0.17587 (19)	0.20310 (8)	0.0286 (4)
C6A	0.18349 (9)	0.1215 (2)	0.19258 (9)	0.0332 (5)
F5B	0.21480 (6)	0.72438 (14)	−0.15032 (5)	0.0419 (3)
O2B	0.46711 (6)	0.54980 (13)	0.09792 (6)	0.0280 (3)
N1B	0.41539 (7)	0.70320 (16)	−0.00875 (7)	0.0278 (3)
N3B	0.33298 (7)	0.53026 (15)	0.02705 (7)	0.0261 (3)
N4B	0.19773 (8)	0.51382 (18)	−0.04738 (8)	0.0328 (4)
C2B	0.40666 (8)	0.59203 (17)	0.04058 (8)	0.0240 (4)
C4B	0.26965 (9)	0.57389 (18)	−0.03540 (8)	0.0259 (4)
C5B	0.27992 (9)	0.68402 (19)	−0.08772 (8)	0.0285 (4)
C6B	0.35239 (9)	0.74902 (19)	−0.07308 (8)	0.0298 (4)
H2A	0.4807 (12)	0.294 (3)	0.1263 (11)	0.037 (5)*
H2B	0.4701 (12)	0.135 (3)	0.0868 (12)	0.042 (5)*
H4A	0.5134 (13)	−0.381 (3)	0.2935 (11)	0.048 (6)*
H4A1	0.3799 (13)	0.308 (3)	0.1947 (11)	0.040 (5)*
H1A	0.07100	0.14180	0.12550	0.0380*
H4A2	0.3380 (13)	0.418 (3)	0.1253 (13)	0.049 (6)*
H6A	0.17710	0.04390	0.22640	0.0400*

H1B	0.46300	0.74610	0.00150	0.0330*
H4B1	0.1965 (13)	0.453 (3)	−0.0107 (12)	0.047 (6)*
H4B2	0.1569 (13)	0.543 (3)	−0.0874 (13)	0.045 (6)*
H6B	0.35960	0.82540	−0.10690	0.0360*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0248 (8)	0.0253 (8)	0.0219 (8)	0.0000	0.0085 (7)	0.0000
N2	0.0389 (8)	0.0345 (8)	0.0244 (7)	−0.0006 (6)	0.0133 (6)	0.0007 (5)
N3	0.0418 (8)	0.0307 (7)	0.0290 (7)	−0.0010 (5)	0.0138 (6)	−0.0013 (5)
N4	0.098 (2)	0.0262 (10)	0.0346 (11)	0.0000	0.0362 (13)	0.0000
C2	0.0196 (6)	0.0293 (7)	0.0231 (7)	0.0011 (5)	0.0064 (5)	−0.0001 (5)
C4	0.0387 (11)	0.0260 (10)	0.0245 (10)	0.0000	0.0124 (9)	0.0000
F5A	0.0276 (5)	0.0583 (7)	0.0320 (5)	0.0010 (4)	0.0043 (4)	0.0153 (4)
O2A	0.0229 (5)	0.0448 (7)	0.0268 (5)	−0.0027 (4)	0.0070 (4)	0.0085 (5)
N1A	0.0245 (6)	0.0405 (7)	0.0289 (7)	−0.0059 (5)	0.0106 (5)	0.0071 (5)
N3A	0.0222 (6)	0.0289 (6)	0.0244 (6)	−0.0020 (5)	0.0096 (5)	0.0018 (5)
N4A	0.0216 (6)	0.0349 (7)	0.0318 (7)	−0.0005 (5)	0.0099 (6)	0.0054 (5)
C2A	0.0245 (7)	0.0299 (7)	0.0219 (7)	−0.0018 (5)	0.0101 (6)	−0.0004 (5)
C4A	0.0250 (7)	0.0249 (7)	0.0239 (7)	−0.0008 (5)	0.0112 (6)	−0.0031 (5)
C5A	0.0261 (7)	0.0334 (8)	0.0226 (7)	0.0005 (6)	0.0065 (6)	0.0033 (6)
C6A	0.0312 (8)	0.0387 (8)	0.0283 (8)	−0.0037 (6)	0.0111 (6)	0.0090 (6)
F5B	0.0300 (5)	0.0569 (6)	0.0302 (5)	−0.0019 (4)	0.0041 (4)	0.0115 (4)
O2B	0.0250 (5)	0.0298 (5)	0.0269 (5)	−0.0040 (4)	0.0085 (4)	0.0023 (4)
N1B	0.0246 (6)	0.0310 (6)	0.0282 (6)	−0.0051 (5)	0.0114 (5)	0.0032 (5)
N3B	0.0245 (6)	0.0270 (6)	0.0279 (6)	−0.0055 (5)	0.0119 (5)	−0.0003 (5)
N4B	0.0258 (7)	0.0408 (8)	0.0294 (7)	−0.0066 (5)	0.0092 (6)	0.0010 (6)
C2B	0.0267 (7)	0.0226 (6)	0.0241 (7)	−0.0030 (5)	0.0119 (6)	−0.0030 (5)
C4B	0.0274 (7)	0.0254 (7)	0.0259 (7)	−0.0032 (5)	0.0122 (6)	−0.0045 (5)
C5B	0.0267 (7)	0.0341 (8)	0.0217 (7)	0.0007 (6)	0.0072 (6)	0.0014 (6)
C6B	0.0320 (8)	0.0328 (8)	0.0257 (7)	−0.0021 (6)	0.0130 (6)	0.0040 (6)

Geometric parameters (Å, º)

F5A—C5A	1.3491 (18)	N4A—C4A	1.331 (2)
F5B—C5B	1.3492 (18)	N1A—H1A	0.8800
O2A—C2A	1.2462 (19)	N4A—H4A2	0.91 (2)
O2B—C2B	1.2539 (19)	N4A—H4A1	0.86 (2)
N1—C2	1.3563 (16)	N1B—C2B	1.3714 (19)
N1—C2^{i}	1.3563 (16)	N1B—C6B	1.361 (2)
N2—C2	1.350 (2)	N3B—C4B	1.338 (2)
N3—C2	1.365 (2)	N3B—C2B	1.356 (2)
N3—C4	1.3751 (18)	N4B—C4B	1.329 (2)
N4—C4	1.346 (3)	N1B—H1B	0.8800
N2—H2A	0.89 (2)	N4B—H4B1	0.88 (2)
N2—H2B	0.84 (2)	N4B—H4B2	0.86 (2)
N4—H4A	0.89 (2)	C4A—C5A	1.426 (2)

N4—H4A^{i}	0.89 (2)	C5A—C6A	1.340 (3)
N1A—C2A	1.376 (2)	C6A—H6A	0.9500
N1A—C6A	1.352 (2)	C4B—C5B	1.423 (2)
N3A—C4A	1.335 (2)	C5B—C6B	1.341 (2)
N3A—C2A	1.356 (2)	C6B—H6B	0.9500
F5A···C2^{i}	3.134 (2)	C4B···C4B^{ix}	3.340 (2)
F5A···C6B^{ii}	3.2444 (19)	C5A···C5B^{v}	3.541 (2)
F5A···N4A	2.7560 (18)	C5B···C6A^{v}	3.432 (2)
F5B···N4B	2.7459 (19)	C5B···C5A^{v}	3.541 (2)
F5B···C6A^{iii}	3.148 (2)	C5B···C4B^{ix}	3.500 (2)
F5A···H4A1	2.47 (2)	C6A···F5B^{ii}	3.148 (2)
F5A···H6B^{ii}	2.4300	C6A···C5B^{v}	3.432 (2)
F5B···H4B2	2.42 (2)	C6B···N3A^{ix}	3.325 (2)
O2A···N1B^{iv}	2.7545 (19)	C6B···F5A^{iii}	3.2444 (19)
O2A···N2^{v}	2.8949 (19)	C6B···N4B^{ix}	3.442 (2)
O2B···N4^{vi}	2.9600 (15)	C2···H4A1	2.69 (2)
O2B···N2	2.9689 (19)	C2···H4A1^{i}	3.03 (2)
O2B···N4^{vii}	2.9600 (15)	C2···H4B2^{v}	2.84 (2)
O2B···N1A^{viii}	2.773 (2)	C2A···H4B1	2.96 (2)
O2A···H1B^{iv}	1.8800	C2A···H6B^{ix}	3.0600
O2A···H2B^{v}	2.15 (2)	C2A···H1B^{iv}	2.7700
O2B···H4A^{vii}	2.09 (2)	C2B···H1A^{viii}	2.8000
O2B···H4A2	2.84 (3)	C2B···H4A^{vii}	2.98 (2)
O2B···H1A^{viii}	1.9000	C2B···H4A2	2.84 (2)
O2B···H2A	2.10 (2)	C2B···H2A	2.90 (2)
N1···N4A	3.0664 (18)	C4A···H6A^{xii}	2.9600
N1···N4A^{i}	3.0664 (18)	H4A1···C2	2.69 (2)
N1A···O2B^{iv}	2.773 (2)	H4A1···N1	2.23 (2)
N1B···O2A^{viii}	2.7545 (19)	H4A1···N2	2.93 (2)
N2···O2B	2.9689 (19)	H4A1···N1	2.23 (2)
N2···O2A^{v}	2.8949 (19)	H4A1···F5A	2.47 (2)
N3A···N4B	3.060 (2)	H4A1···C2^{i}	3.03 (2)
N3A···C6B^{ix}	3.325 (2)	H1A···C2B^{iv}	2.8000
N3B···N4A	2.992 (2)	H1A···H1B^{iv}	2.5600
N4···O2B^{x}	2.9600 (15)	H1A···O2B^{iv}	1.9000
N4···O2B^{xi}	2.9600 (15)	H1B···C2A^{viii}	2.7700
N4A···N1	3.0664 (18)	H1B···O2A^{viii}	1.8800
N4A···N1	3.0664 (18)	H1B···H1A^{viii}	2.5600
N4A···C2	3.356 (2)	H4A2···O2B	2.84 (3)
N4A···N3B	2.992 (2)	H4A2···N3B	2.10 (2)
N4A···F5A	2.7560 (18)	H4A2···C2B	2.84 (2)
N4B···C4A^{v}	3.442 (2)	H2A···C2B	2.90 (2)
N4B···N3A	3.060 (2)	H2A···O2B	2.10 (2)
N4B···F5B	2.7459 (19)	H2B···O2A^{v}	2.15 (2)
N4B···C6B^{ix}	3.442 (2)	H4B1···N3A	2.20 (2)
N1···H4A1	2.23 (2)	H4B1···C2A	2.96 (2)
N1···H4A1^{i}	2.23 (2)	H4B2···F5B	2.42 (2)

N2···H4A1	2.93 (2)	H4B2···N3^{v}	2.53 (2)
N3···H4B2^{v}	2.53 (2)	H4B2···C2^{v}	2.84 (2)
N3A···H6B^{ix}	2.8700	H4A···O2B^{x}	2.09 (2)
N3A···H4B1	2.20 (2)	H4A···C2B^{x}	2.98 (2)
N3B···H4A2	2.10 (2)	H6A···N4A^{xiii}	2.7700
N4A···H6A^{xii}	2.7700	H6A···C4A^{xiii}	2.9600
C2···N4A	3.356 (2)	H6B···F5A^{iii}	2.4300
C2···F5A^{i}	3.134 (2)	H6B···N3A^{ix}	2.8700
C4A···N4B^{v}	3.442 (2)	H6B···C2A^{ix}	3.0600
C4B···C5B^{ix}	3.500 (2)		

C2—N1—C2^{i}	115.16 (14)	N3—C4—N3^{i}	122.49 (19)
C2—N3—C4	116.06 (14)	N3—C4—N4	118.75 (11)
C2—N2—H2B	119.3 (16)	O2A—C2A—N1A	119.37 (15)
H2A—N2—H2B	115 (2)	N1A—C2A—N3A	119.33 (14)
C2—N2—H2A	121.7 (13)	O2A—C2A—N3A	121.30 (14)
C4—N4—H4A	118.2 (15)	N3A—C4A—N4A	119.11 (14)
H4A—N4—H4A^{i}	124 (2)	N3A—C4A—C5A	120.14 (15)
C4—N4—H4A^{i}	118.2 (15)	N4A—C4A—C5A	120.73 (14)
C2A—N1A—C6A	122.07 (15)	F5A—C5A—C6A	121.59 (14)
C2A—N3A—C4A	119.96 (13)	F5A—C5A—C4A	118.77 (15)
C6A—N1A—H1A	119.00	C4A—C5A—C6A	119.64 (15)
C2A—N1A—H1A	119.00	N1A—C6A—C5A	118.83 (15)
C4A—N4A—H4A1	121.3 (16)	N1A—C6A—H6A	121.00
C4A—N4A—H4A2	116.3 (16)	C5A—C6A—H6A	121.00
H4A1—N4A—H4A2	120 (2)	O2B—C2B—N3B	120.96 (14)
C2B—N1B—C6B	121.81 (14)	N1B—C2B—N3B	119.73 (14)
C2B—N3B—C4B	119.92 (13)	O2B—C2B—N1B	119.31 (14)
C2B—N1B—H1B	119.00	N3B—C4B—C5B	119.89 (16)
C6B—N1B—H1B	119.00	N4B—C4B—C5B	120.96 (15)
C4B—N4B—H4B2	119.0 (17)	N3B—C4B—N4B	119.15 (14)
H4B1—N4B—H4B2	126 (2)	C4B—C5B—C6B	120.04 (14)
C4B—N4B—H4B1	114.6 (16)	F5B—C5B—C4B	118.25 (15)
N2—C2—N3	119.01 (13)	F5B—C5B—C6B	121.68 (14)
N1—C2—N2	116.19 (14)	N1B—C6B—C5B	118.54 (14)
N1—C2—N3	124.81 (13)	N1B—C6B—H6B	121.00
N3^{i}—C4—N4	118.75 (11)	C5B—C6B—H6B	121.00

C2^{i}—N1—C2—N2	−176.73 (13)	C4B—N3B—C2B—O2B	−178.38 (14)
C2^{i}—N1—C2—N3	3.98 (19)	C2B—N3B—C4B—N4B	−179.21 (14)
C4—N3—C2—N1	−7.5 (2)	C2B—N3B—C4B—C5B	0.5 (2)
C4—N3—C2—N2	173.24 (13)	C4B—N3B—C2B—N1B	2.1 (2)
C2—N3—C4—N4	−176.55 (11)	N3A—C4A—C5A—F5A	179.63 (13)
C2—N3—C4—N3^{i}	3.45 (18)	N3A—C4A—C5A—C6A	−0.1 (2)
C6A—N1A—C2A—O2A	−177.48 (15)	N4A—C4A—C5A—F5A	−2.1 (2)
C6A—N1A—C2A—N3A	2.2 (2)	N4A—C4A—C5A—C6A	178.19 (15)
C2A—N1A—C6A—C5A	−1.3 (2)	F5A—C5A—C6A—N1A	−179.48 (14)
C4A—N3A—C2A—O2A	177.67 (14)	C4A—C5A—C6A—N1A	0.3 (2)

C4A—N3A—C2A—N1A	−2.0 (2)	N3B—C4B—C5B—F5B	179.56 (14)
C2A—N3A—C4A—N4A	−177.35 (14)	N3B—C4B—C5B—C6B	−2.6 (2)
C2A—N3A—C4A—C5A	1.0 (2)	N4B—C4B—C5B—F5B	−0.8 (2)
C6B—N1B—C2B—N3B	−2.7 (2)	N4B—C4B—C5B—C6B	177.13 (15)
C2B—N1B—C6B—C5B	0.6 (2)	F5B—C5B—C6B—N1B	179.78 (14)
C6B—N1B—C2B—O2B	177.75 (14)	C4B—C5B—C6B—N1B	2.0 (2)

Symmetry codes: (i) −*x*+1, *y*, −*z*+1/2; (ii) *x*, −*y*+1, *z*+1/2; (iii) *x*, −*y*+1, *z*−1/2; (iv) *x*−1/2, *y*−1/2, *z*; (v) −*x*+1/2, −*y*+1/2, −*z*; (vi) *x*, *y*+1, *z*; (vii) −*x*+1, *y*+1, −*z*+1/2; (viii) *x*+1/2, *y*+1/2, *z*; (ix) −*x*+1/2, −*y*+3/2, −*z*; (x) −*x*+1, *y*−1, −*z*+1/2; (xi) *x*, *y*−1, *z*; (xii) −*x*+1/2, *y*+1/2, −*z*+1/2; (xiii) −*x*+1/2, *y*−1/2, −*z*+1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4*A*—H4*A*1···F5*A*	0.86 (2)	2.47 (2)	2.7560 (18)	100.0 (18)
N4*A*—H4*A*1···N1	0.86 (2)	2.23 (2)	3.0664 (18)	164 (2)
N1*A*—H1*A*···O2*B*^{iv}	0.88	1.90	2.773 (2)	173
N1*B*—H1*B*···O2*A*^{viii}	0.88	1.88	2.7545 (19)	175
N4*A*—H4*A*2···N3*B*	0.91 (2)	2.10 (2)	2.992 (2)	169 (2)
N2—H2*A*···O2*B*	0.89 (2)	2.10 (2)	2.9689 (19)	167.6 (18)
N2—H2*B*···O2*A*^{v}	0.84 (2)	2.15 (2)	2.8949 (19)	149 (2)
N4*B*—H4*B*1···N3*A*	0.88 (2)	2.20 (2)	3.060 (2)	169 (2)
N4*B*—H4*B*2···F5*B*	0.86 (2)	2.42 (2)	2.7459 (19)	103 (2)
N4*B*—H4*B*2···N3^{v}	0.86 (2)	2.53 (2)	3.360 (2)	162 (2)
N4—H4*A*···O2*B*^{x}	0.89 (2)	2.09 (2)	2.9600 (15)	165 (2)
C6*B*—H6*B*···F5*A*^{iii}	0.95	2.43	3.2444 (19)	143

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