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Hydrogen-bonding patterns in pyrimethamine tetrafluoroborate

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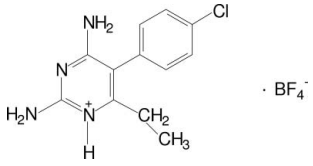
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.003 Å; R factor = 0.045; wR factor = 0.126; data-to-parameter ratio = 17.2.

The title compound [systematic name: 2,4-diamino-5-(4-chlorophenyl)-6-ethylpyrimdinium tetrafluoroborate], $C_{12}H_{14}ClN_4^+\cdot BF_4^-$, is isomorphous with pyrimethamine perchlorate. The pyrimethamine (PMN) molecule is protonated at one of the pyrimidine N atoms. The protonated N atom and 2-amino group of the PMN cation interact with the tetrafluoroborate anion through a pair of N—H···F hydrogen bonds [graph set $R_2^2(8)$]. The inversion-related PMN cations are linked through a pair of N—H···N hydrogen bonds. In addition to the base pairing, the F atoms bridge the 2-amino and 4-amino groups on either side of the paired bases, resulting in a complementary DADA array.

Related literature

For related literature, see: Balasubramani *et al.* (2005); Bernstein *et al.* (1995); Etter (1990); Hemamalini *et al.* (2005); Lynch & Jones (2004); Muthiah *et al.* (2002); Olliaro (2001); Sethuraman & Muthiah (2002); Sethuraman (2002); Stanley *et al.* (2005).



Experimental

Crystal data

$C_{12}H_{14}ClN_4^+\cdot BF_4^-$
M_r = 336.53
Monoclinic, $P2_1/c$
a = 8.3042 (2) Å
b = 13.2529 (4) Å
c = 13.7368 (4) Å
β = 97.326 (2)°
V = 1499.46 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.30 mm^{-1}
T = 120 K
0.25 × 0.20 × 0.15 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.929, T_{max} = 0.957
13025 measured reflections
3436 independent reflections
2654 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.126
S = 1.07
3436 reflections
200 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···F4	0.86	1.91	2.7609 (19)	171
N2—H2A···F1^{i}	0.86	2.10	2.9537 (18)	172
N2—H2B···F3	0.86	2.27	3.019 (2)	146
N4—H4A···N3^{ii}	0.86	2.24	3.033 (2)	154
N4—H4B···F1^{iii}	0.86	2.22	2.8561 (18)	130
C8—H8B···F4^{iv}	0.96	2.50	3.345 (3)	147
C14—H14···F2^{v}	0.93	2.55	3.444 (2)	162

Symmetry codes: (i) $-x+2, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+1, -y, -z+1$; (iii) $x-1, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $-x+2, -y+1, -z+1$; (v) $x, -y+\frac{1}{2}, z-\frac{1}{2}$.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

DL thanks the EPSRC National Crystallography Service (Southampton, England) for the X-ray data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2329).

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supplementary materials

Acta Cryst. (2007). E**63**, o2966 [**doi:10.1107/S1600536807015656**]

Hydrogen-bonding patterns in pyrimethamine tetrafluoroborate

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Comment

Pyrimethamine [2,4-diamino-5-(*p*-chlorophenyl)-6-ethylpyrimidine] is an antifolate drug used in anti-malarial chemotherapy (Olliaro, 2001). The crystal structure of pyrimethamine (PMN) itself has been reported from our laboratory (Sethuraman & Muthiah, 2002). The present study has been undertaken to explore the hydrogen bonding patterns involving the PMN cation in a variety of environments. The crystal structures of trimethoprim tetrafluoridoborate (Hemamalini *et al.*, 2005) and PMN dinitrate (Balasubramani *et al.*, 2005) have also been reported from our laboratory.

The asymmetric unit of (I) contains a protonated pyrimethamine (PMN) cation and a tetrafluoridoborate anion (FLUB) (Fig.1). The pyrimethamine molecule is protonated at atom N1 of the pyrimidine moiety, which is evident from the increase in the internal angle at protonated N1 (C2—N1—C6 = 121.99 (14) Å) compared with that at unprotanated atom N3(C2—N3—C4 = 117.90 (15) Å). The dihedral angle between the pyrimidine and benzene planes is 67.79 (8) Å. The torsion angle (C5—C6—C7—C8) is 106.3 (2) Å. The distorted tetrahedral BF_4 ion has typical B—F distances.

The protonated atom N1 and the 2-amino group is hydrogen bonded to the F atoms of the tetrafluoridoborate anions (F3 & F4) leading to the formation of a fork-like hydrogen bonding pattern with graph-set notation $R^2_2(8)$ (Etter, 1990; Bernstein *et al.*, 1995). The $R^2_2(8)$ motif is frequently observed in aminopyrimidine carboxylate salts (Lynch & Jones, 2004). Here the tetrafluoridoborate anion mimics the role of the carboxylate group. The PMN cations are centrosymmetrically paired through N—H···N hydrogen bonds involving the 4-amino group and the N3 atom of the unprotonated pyrimidine to form the ring motif $R^2_2(8)$. The pairs further interact with tetrafluoridoborate anion through N—H···F hydrogen bonds. The fluorine atom (F3) connects the 2-amino and 4-amino groups on either side of the paired PMN cation, forming an eight membered hydrogen bonded ring motif with graph set $R^3_2(8)$. This pattern is called a complementary DADA (D is donor and A is acceptor) array of quadruple hydrogen bonds (Fig.2). The DADA array of cyclic hydrogen-bonded ring motifs can be represented by graph set notations $R^3_2(8)$, $R^2_2(8)$ and $R^3_2(8)$. This pattern is similar to that reported in PMN carboxylates (Stanley *et al.*, 2005).

The present crystal structure is isomorphous with pyrimethamine perchlorate (Sethuraman, 2002). This is very interesting from crystal engineering point of view. Since both the anions, (perchlorate and tetrafluoridoborate) have a tetrahedral geometry and similar hydrogen bonding capability (hydrogen bond acceptors). Trimethoprim perchlorate (Muthiah *et al.*, 2002) and trimethoprim tetrafluoridoborate (Hemamalini *et al.*, 2005) are also isomorphous.

Experimental

Hot methanolic solution of pyrimethamine (30 mg, Aldrich), and tetrafluoridoboric acid (220 mg of 40% solution; Aldrich) were mixed in a 1:2 molar ratio. The resulting solution was warmed over a water bath for a few minutes and then kept at room temperature for crystallization. After a few days crystals appeared from the mother liquor.

Refinement

All the H atoms were fixed geometrically and were refined using a riding model. with N—H = 0.86Å and C—H ranging from 0.93 to 0.97Å and with U_{iso}(H)=1.2Ueq(C,*N*).

Figures

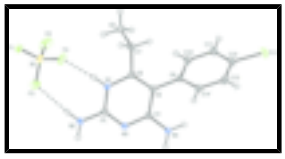

Fig. 1. A view of (I), with the atom-labelling scheme and 50% probability displacement ellipsoids

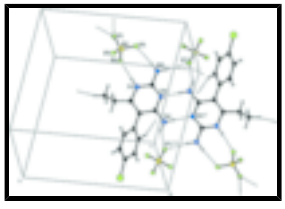

Fig. 2. A view of the hydrogen-bonded supramolecular chain in (I) Symmetry codes:(i)2 − *x*,*y* − 1/2,3/2 − *z*;(ii)1 − *x*,-*y*,1 − *z*;(iii)*x* − 1,1/2 − *y*,*z* − 1/2;

'2,4-diamino-5-(*p*-chlorophenyl)-6-ethylpyrimidinium tetrafluoridoborate'

Crystal data

$C_{12}H_{14}ClN_4^+ \cdot BF_4^-$	F_{000} = 688
M_r = 336.53	D_x = 1.491 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 3445 reflections
a = 8.3042 (2) Å	θ = 2.1–27.6°
b = 13.2529 (4) Å	μ = 0.30 mm^{-1}
c = 13.7368 (4) Å	*T* = 120 K
β = 97.326 (2)°	Block, colourless
V = 1499.46 (7) Å^3	0.25 × 0.20 × 0.15 mm
Z = 4	

Data collection

Bruker–Nonius KappaCCD diffractometer	3436 independent reflections
Radiation source: Bruker–Nonius FR591 rotating anode	2654 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.033
Detector resolution: 9.091 pixels mm^{-1}	θ_{max} = 27.6°
T = 120(2) K	θ_{min} = 2.1°
φ&ω scans	*h* = −10→10
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	*k* = −16→17

T_{min} = 0.929, T_{max} = 0.957
13025 measured reflections

l = −17→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.126
S = 1.07
3436 reflections
200 parameters
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0697P)^2 + 0.5139P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}
Extinction correction: none

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All e.s.d.'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 $F^2 > 2\text{sigma}(F^2)$ 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}
Cl1	0.20890 (6)	0.30756 (4)	−0.01027 (3)	0.0335 (2)
N1	0.81272 (17)	0.24830 (10)	0.51009 (10)	0.0187 (4)
N2	0.86615 (18)	0.13132 (11)	0.63404 (11)	0.0229 (4)
N3	0.67182 (17)	0.09490 (11)	0.50368 (11)	0.0180 (4)
N4	0.47915 (17)	0.06149 (11)	0.37458 (11)	0.0204 (4)
C2	0.7825 (2)	0.15724 (13)	0.54826 (13)	0.0181 (5)
C4	0.5906 (2)	0.12414 (12)	0.41709 (12)	0.0167 (5)
C5	0.6199 (2)	0.21960 (12)	0.37222 (13)	0.0169 (5)
C6	0.7337 (2)	0.28059 (12)	0.42153 (13)	0.0176 (5)
C7	0.7823 (2)	0.38326 (13)	0.39047 (14)	0.0223 (5)
C8	0.7174 (3)	0.46708 (14)	0.45136 (16)	0.0309 (6)
C9	0.5242 (2)	0.24697 (13)	0.27664 (12)	0.0178 (5)
C10	0.4071 (2)	0.32305 (14)	0.27008 (14)	0.0227 (5)
C11	0.3121 (2)	0.34435 (14)	0.18187 (14)	0.0245 (5)
C12	0.3328 (2)	0.28714 (14)	0.09990 (14)	0.0231 (5)
C13	0.4498 (2)	0.21222 (14)	0.10388 (13)	0.0227 (5)

C14	0.5453 (2)	0.19232 (13)	0.19203 (14)	0.0213 (5)
F1	1.15948 (13)	0.43382 (8)	0.76949 (8)	0.0282 (3)
F2	0.88796 (16)	0.45512 (11)	0.73877 (14)	0.0630 (6)
F3	0.99045 (17)	0.29803 (9)	0.77354 (10)	0.0464 (5)
F4	1.01944 (16)	0.37203 (10)	0.62986 (9)	0.0469 (5)
B1	1.0123 (3)	0.38982 (16)	0.73014 (16)	0.0249 (6)
H1	0.88350	0.28720	0.54220	0.0220*
H2A	0.84830	0.07420	0.66040	0.0270*
H2B	0.93790	0.17170	0.66300	0.0270*
H4A	0.46140	0.00510	0.40230	0.0240*
H4B	0.42440	0.07710	0.31920	0.0240*
H7A	0.74150	0.39330	0.32180	0.0270*
H7B	0.89980	0.38730	0.39720	0.0270*
H8A	0.60080	0.46580	0.44200	0.0460*
H8B	0.75460	0.53130	0.43080	0.0460*
H8C	0.75580	0.45680	0.51960	0.0460*
H10	0.39250	0.36010	0.32580	0.0270*
H11	0.23590	0.39610	0.17780	0.0290*
H13	0.46410	0.17560	0.04790	0.0270*
H14	0.62410	0.14220	0.19500	0.0260*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0249 (3)	0.0522 (3)	0.0218 (3)	−0.0043 (2)	−0.0031 (2)	0.0113 (2)
N1	0.0171 (7)	0.0176 (7)	0.0205 (8)	−0.0039 (6)	−0.0016 (6)	−0.0009 (6)
N2	0.0238 (8)	0.0214 (7)	0.0215 (8)	−0.0038 (6)	−0.0051 (6)	0.0029 (6)
N3	0.0169 (7)	0.0174 (7)	0.0192 (7)	−0.0004 (6)	0.0000 (6)	0.0006 (6)
N4	0.0220 (8)	0.0178 (7)	0.0199 (8)	−0.0042 (6)	−0.0026 (6)	0.0027 (6)
C2	0.0164 (8)	0.0181 (8)	0.0197 (9)	0.0006 (7)	0.0020 (7)	−0.0002 (7)
C4	0.0155 (8)	0.0165 (8)	0.0185 (8)	0.0018 (6)	0.0033 (6)	−0.0009 (6)
C5	0.0167 (8)	0.0169 (8)	0.0174 (8)	0.0009 (6)	0.0030 (7)	0.0005 (6)
C6	0.0167 (8)	0.0171 (8)	0.0194 (8)	0.0016 (6)	0.0039 (7)	0.0014 (6)
C7	0.0235 (9)	0.0196 (8)	0.0237 (9)	−0.0036 (7)	0.0023 (7)	0.0029 (7)
C8	0.0388 (11)	0.0187 (9)	0.0359 (11)	−0.0012 (8)	0.0069 (9)	0.0018 (8)
C9	0.0169 (8)	0.0174 (8)	0.0191 (9)	−0.0028 (6)	0.0018 (7)	0.0028 (7)
C10	0.0231 (9)	0.0231 (9)	0.0221 (9)	0.0010 (7)	0.0031 (7)	−0.0004 (7)
C11	0.0207 (9)	0.0249 (9)	0.0274 (10)	0.0020 (7)	0.0009 (7)	0.0053 (8)
C12	0.0190 (9)	0.0299 (10)	0.0198 (9)	−0.0062 (7)	0.0003 (7)	0.0072 (7)
C13	0.0228 (9)	0.0285 (9)	0.0173 (9)	−0.0053 (8)	0.0040 (7)	−0.0001 (7)
C14	0.0197 (9)	0.0218 (8)	0.0228 (9)	−0.0008 (7)	0.0039 (7)	0.0009 (7)
F1	0.0239 (6)	0.0281 (6)	0.0297 (6)	−0.0050 (4)	−0.0072 (5)	−0.0034 (5)
F2	0.0286 (7)	0.0495 (9)	0.1086 (14)	0.0075 (6)	0.0004 (8)	−0.0334 (9)
F3	0.0533 (8)	0.0382 (7)	0.0464 (9)	−0.0196 (6)	0.0009 (7)	0.0058 (6)
F4	0.0515 (8)	0.0565 (9)	0.0311 (7)	−0.0261 (7)	−0.0013 (6)	−0.0129 (6)
B1	0.0215 (10)	0.0245 (10)	0.0280 (12)	−0.0011 (8)	−0.0001 (9)	−0.0071 (9)

Geometric parameters (Å, °)

Cl1—C12	1.7393 (19)	C5—C6	1.357 (2)
F1—B1	1.399 (3)	C6—C7	1.497 (2)
F2—B1	1.364 (3)	C7—C8	1.529 (3)
F3—B1	1.377 (2)	C9—C10	1.396 (2)
F4—B1	1.406 (3)	C9—C14	1.399 (2)
N1—C6	1.375 (2)	C10—C11	1.388 (3)
N1—C2	1.352 (2)	C11—C12	1.386 (3)
N2—C2	1.334 (2)	C12—C13	1.385 (3)
N3—C2	1.326 (2)	C13—C14	1.386 (3)
N3—C4	1.347 (2)	C7—H7A	0.9700
N4—C4	1.323 (2)	C7—H7B	0.9698
N1—H1	0.8601	C8—H8A	0.9605
N2—H2A	0.8601	C8—H8B	0.9601
N2—H2B	0.8598	C8—H8C	0.9606
N4—H4A	0.8600	C10—H10	0.9302
N4—H4B	0.8603	C11—H11	0.9300
C4—C5	1.441 (2)	C13—H13	0.9297
C5—C9	1.490 (2)	C14—H14	0.9297
Cl1···F3^{i}	3.2791 (14)	C14···N4	3.154 (2)
Cl1···N1^{ii}	3.4183 (15)	C2···H4A^{xi}	3.0892
Cl1···N4^{iii}	3.3846 (15)	C4···H4A^{xi}	3.0901
Cl1···C4^{iii}	3.5593 (17)	C6···H13^{vii}	3.0584
Cl1···H1^{ii}	3.1457	C8···H1	2.9502
F1···N4^{iv}	2.8561 (18)	C9···H4B	2.4941
F1···C7^{v}	3.348 (2)	C9···H7A	2.6677
F1···N2^{vi}	2.9537 (18)	C10···H7A	2.9291
F3···C6^{vii}	3.297 (2)	C11···H2B^{ii}	3.0924
F3···Cl1^{viii}	3.2791 (14)	C13···H8B^{xiii}	2.9412
F3···N2	3.019 (2)	C14···H4B	2.6151
F4···C8^{v}	3.345 (3)	B1···H2A^{vi}	3.0213
F4···N1	2.7609 (19)	B1···H1	2.9924
F1···H2A^{vi}	2.0997	H1···C8	2.9502
F1···H7A^{v}	2.7859	H1···B1	2.9924
F1···H4B^{iv}	2.2235	H1···F4	1.9083
F2···H11^{ix}	2.5612	H1···Cl1^{iv}	3.1457
F2···H14^{vii}	2.5476	H1···H2B	2.2604
F3···H2B	2.2650	H1···H7B	2.4113
F4···H1	1.9083	H1···H8C	2.4878
F4···H2B	2.7916	H2A···B1^{x}	3.0213
F4···H8B^{v}	2.5011	H2A···H7A^{vii}	2.5277
F4···H8C	2.7393	H2A···F1^{x}	2.0997
N1···Cl1^{iv}	3.4183 (15)	H2B···F3	2.2650

N1···F4	2.7609 (19)	H2B···F4	2.7916
N2···F3	3.019 (2)	H2B···H1	2.2604
N2···F1^{x}	2.9537 (18)	H2B···C11^{iv}	3.0924
N3···N4^{xi}	3.033 (2)	H4A···C2^{xi}	3.0892
N4···Cl1^{vii}	3.3846 (15)	H4A···C4^{xi}	3.0901
N4···N3^{xi}	3.033 (2)	H4A···N3^{xi}	2.2389
N4···C14	3.154 (2)	H4B···C9	2.4941
N4···F1^{ii}	2.8561 (18)	H4B···C14	2.6151
N1···H8C	2.8092	H4B···F1^{ii}	2.2235
N2···H7A^{vii}	2.9174	H7A···N2^{iii}	2.9174
N3···H4A^{xi}	2.2389	H7A···C9	2.6677
C2···C14^{vii}	3.570 (2)	H7A···H2A^{iii}	2.5277
C2···C13^{vii}	3.428 (2)	H7A···F1^{v}	2.7859
C4···Cl1^{vii}	3.5593 (17)	H7A···C10	2.9291
C6···F3^{iii}	3.297 (2)	H7B···H1	2.4113
C7···C10	3.430 (2)	H8B···C13^{xii}	2.9412
C7···F1^{v}	3.348 (2)	H8B···F4^{v}	2.5011
C8···F4^{v}	3.345 (3)	H8C···F4	2.7393
C8···C13^{xii}	3.576 (3)	H8C···N1	2.8092
C10···C7	3.430 (2)	H8C···H1	2.4878
C13···C8^{xiii}	3.576 (3)	H11···F2^{ix}	2.5612
C13···C2^{iii}	3.428 (2)	H13···C6^{iii}	3.0584
C14···C2^{iii}	3.570 (2)	H14···F2^{iii}	2.5476
C2—N1—C6	121.99 (14)	Cl1—C12—C13	118.68 (14)
C2—N3—C4	117.90 (15)	C11—C12—C13	121.26 (17)
C2—N1—H1	118.99	C12—C13—C14	119.42 (17)
C6—N1—H1	119.02	C9—C14—C13	120.60 (16)
C2—N2—H2A	120.01	C6—C7—H7A	109.18
C2—N2—H2B	120.03	C6—C7—H7B	109.12
H2A—N2—H2B	119.97	C8—C7—H7A	109.18
H4A—N4—H4B	119.96	C8—C7—H7B	109.16
C4—N4—H4A	119.99	H7A—C7—H7B	107.91
C4—N4—H4B	120.04	C7—C8—H8A	109.48
N1—C2—N3	121.94 (16)	C7—C8—H8B	109.51
N2—C2—N3	119.97 (16)	C7—C8—H8C	109.54
N1—C2—N2	118.09 (15)	H8A—C8—H8B	109.45
N3—C4—N4	116.91 (15)	H8A—C8—H8C	109.37
N3—C4—C5	122.49 (15)	H8B—C8—H8C	109.49
N4—C4—C5	120.59 (15)	C9—C10—H10	119.41
C4—C5—C6	117.00 (16)	C11—C10—H10	119.46
C4—C5—C9	119.35 (15)	C10—C11—H11	120.60
C6—C5—C9	123.64 (15)	C12—C11—H11	120.56
N1—C6—C5	118.66 (15)	C12—C13—H13	120.29
N1—C6—C7	114.81 (14)	C14—C13—H13	120.28
C5—C6—C7	126.52 (16)	C9—C14—H14	119.69

C6—C7—C8	112.20 (15)	C13—C14—H14	119.71
C5—C9—C10	121.44 (15)	F1—B1—F2	109.61 (16)
C5—C9—C14	119.78 (15)	F1—B1—F3	110.97 (17)
C10—C9—C14	118.70 (16)	F1—B1—F4	107.73 (17)
C9—C10—C11	121.13 (17)	F2—B1—F3	112.33 (19)
C10—C11—C12	118.84 (16)	F2—B1—F4	108.57 (18)
Cl1—C12—C11	120.05 (14)	F3—B1—F4	107.48 (16)
C6—N1—C2—N2	179.16 (15)	C4—C5—C6—N1	−0.2 (2)
C6—N1—C2—N3	−1.8 (3)	C4—C5—C9—C14	−66.9 (2)
C2—N1—C6—C5	1.3 (2)	C6—C5—C9—C10	−69.2 (2)
C2—N1—C6—C7	−179.94 (15)	C6—C5—C9—C14	114.1 (2)
C4—N3—C2—N1	1.1 (2)	C5—C6—C7—C8	106.3 (2)
C4—N3—C2—N2	−179.85 (15)	N1—C6—C7—C8	−72.4 (2)
C2—N3—C4—N4	−179.05 (15)	C5—C9—C10—C11	−176.36 (16)
C2—N3—C4—C5	0.0 (2)	C14—C9—C10—C11	0.4 (3)
N4—C4—C5—C9	−0.5 (2)	C5—C9—C14—C13	175.67 (16)
N3—C4—C5—C6	−0.4 (2)	C10—C9—C14—C13	−1.1 (3)
N3—C4—C5—C9	−179.53 (15)	C9—C10—C11—C12	1.3 (3)
N4—C4—C5—C6	178.56 (16)	C10—C11—C12—C13	−2.4 (3)
C9—C5—C6—N1	178.87 (15)	C10—C11—C12—Cl1	176.78 (14)
C9—C5—C6—C7	0.2 (3)	C11—C12—C13—C14	1.6 (3)
C4—C5—C9—C10	109.79 (19)	Cl1—C12—C13—C14	−177.51 (14)
C4—C5—C6—C7	−178.82 (16)	C12—C13—C14—C9	0.1 (3)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···F4	0.86	1.91	2.7609 (19)	171
N2—H2A···F1^{x}	0.86	2.10	2.9537 (18)	172
N2—H2B···F3	0.86	2.27	3.019 (2)	146
N4—H4A···N3^{xi}	0.86	2.24	3.033 (2)	154
N4—H4B···F1^{ii}	0.86	2.22	2.8561 (18)	130
C8—H8B···F4^{v}	0.96	2.50	3.345 (3)	147
C14—H14···F2^{iii}	0.93	2.55	3.444 (2)	162

Symmetry codes: (x) −*x*+2, *y*−1/2, −*z*+3/2; (xi) −*x*+1, −*y*, −*z*+1; (ii) *x*−1, −*y*+1/2, *z*−1/2; (v) −*x*+2, −*y*+1, −*z*+1; (iii) *x*, −*y*+1/2, *z*−1/2.

Fig. 1

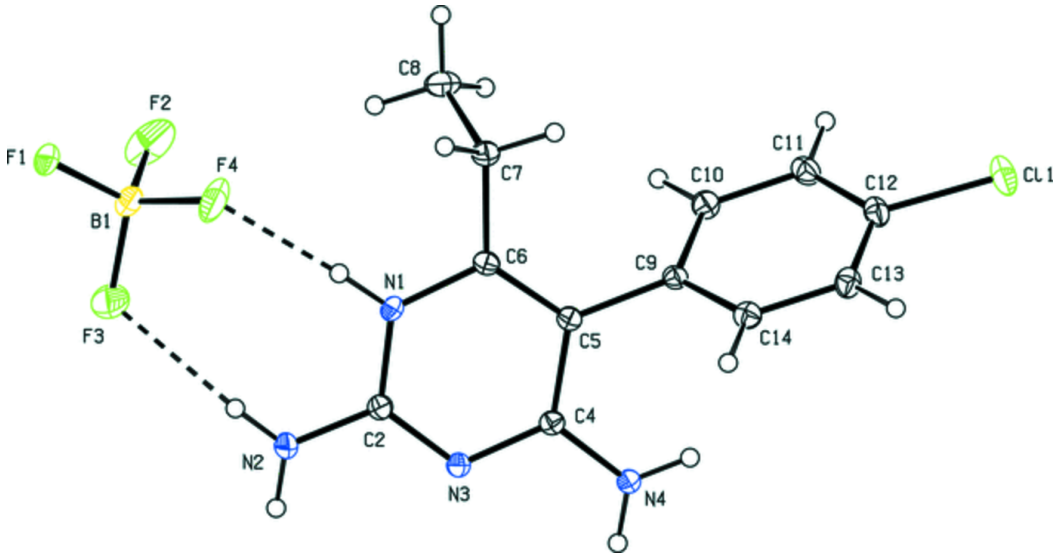
C8
F2
F1
F4
C7
C11
C10
C12
Cl1
B1
C6
C9
N1
C13
F3
C5
C14
C4
C2
N2
N3
N4

Fig. 2