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2,4-Diamino-5-(4-chlorophenyl)-6-ethylpyrimidin-1-ium 2-propanamidobenzoate

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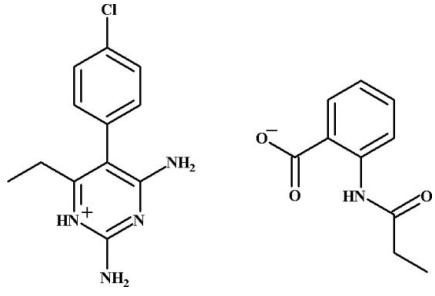
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; R factor = 0.088; wR factor = 0.228; data-to-parameter ratio = 18.1.

In the title salt, $C_{12}H_{14}ClN_4^+\cdot C_{10}H_{10}NO_3^-$, zwitterionic N—H···O interactions form an $R_2^2(8)$ ring. The crystal structure is stabilized by N—H···O and N—H···N hydrogen bonds involving two different eight-membered rings. An N—H···O interaction occurs between the pyrimidine ring (donor) and carboxylate group (acceptor) while the other ring is formed by N—H···N interactions, which form a dimer between two symmetry-related salts. An intramolecular N—H···O hydrogen bond forms a six-membered ring in the benzoate. Intermolecular C—H···O interactions are also observed.

Related literature

For aminopyrimidine carboxylates, see: Chinnakali *et al.* (1999); Lynch & Jones (2004); Stanley *et al.* (2005). For aminopyrimidine and benzoic acid adducts, see: Balasubramani *et al.* (2005, 2006); Thanigaimani *et al.* (2006, 2007). For hydrogen bonding in molecular recognition and crystal engineering, see: Desiraju (1989). For puckering and asymmetry parameters, see: Cremer & Pople, (1975); Nardelli (1995).



Experimental

Crystal data

$C_{12}H_{14}ClN_4^+\cdot C_{10}H_{10}NO_3^-$ M_r = 441.91
Monoclinic, $C2/c$
a = 22.144 (3) Å
b = 9.4915 (14) Å
c = 21.844 (3) Å
β = 99.071 (3)°
V = 4533.7 (12) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.20 mm^{-1}
T = 293 K
0.50 × 0.45 × 0.42 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
17933 measured reflections
5077 independent reflections
2719 reflections with $I > 2\sigma(I)$
R_{int} = 0.039

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.088
$wR(F^2)$ = 0.228
S = 1.06
5077 reflections
281 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5···O2	0.86	1.89	2.605 (4)	140
N2—H2A···O3^{i}	0.86	2.15	2.977 (4)	163
N4—H4A···N1^{ii}	0.86	2.16	2.988 (4)	163
N3—H3···O1^{iii}	0.86	1.80	2.660 (4)	178
C14—H14C···O1^{iii}	0.96	2.53	3.323 (6)	140
N2—H2B···O2^{iii}	0.86	1.91	2.746 (4)	164
N4—H4B···O3^{iv}	0.86	2.35	3.017 (3)	134

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FF2025).

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supporting information

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2,4-Diamino-5-(4-chlorophenyl)-6-ethylpyrimidin-1-ium 2-propanamidobenzoate

Sampath Natarajan and Rita Mathews

S1. Comment

Aminopyrimidine-Carboxylate interactions are important since they are involved in protein-nucleic acids recognition and protein-drug binding. Hydrogen bonding plays a key role in molecular recognition and crystal engineering research (Desiraju, 1989). In general, aminopyrimidines posses self complementary hydrogen-bonded motifs forming a base pair which itself is a unique property. The adducts of carboxylic acid with 2-aminopyrimidine system form a graph-set motif $R_2^2(8)$ (Lynch & Jones, 2004). This motif is very robust in aminopyrimidine-carboxylic acid/carboxylates systems. The crystal structures of many aminopyrimidine carboxylates (Stanley *et al.*, 2005) and co-crystal structures (Chinnakali *et al.*,1999) have been reported. Many structures of aminopyrimidine and benzoic acid adducts are also have been reported. Few of them are 2-amino-4,6-dimethoxy pyrimidine: 4-aminobenzoic acid (Thanigaimani *et al.*, 2006), 2-amino-4,6-dimethoxypyrimidine: phthalic acid (Thanigaimani *et al.*, 2007), 2-amino-4,6-dimethylpyrimidine: cinnamic acid (Balasubramani *et al.*, 2005) and 2-amino-4,6-dimethylpyrimidine: 4-hydroxybenzoic acid (Balasubramani *et al.*, 2006). All these reported structures have common features of heterosynthone formation. In the present study we report a salt (1:1) namely, 2,4-diamino-5-(4-chlorophenyl)-6-ethylpyrimidin-1-ium 2-propanamidobenzoate which forms a zwitterionic interaction between the molecules of aminopyrimidine and benzoate exhibit a motif $R_2^2(8)$ ring.

The asymmetric unit of crystal contains a single molecule of each component of salt (Fig. 1). Interactions are found between the salt of aminopyrimidin-1-ium and benzoate *via* hydrogen bonds N2—H2B···O2 and N3—H3···O1 (Fig. 2). Here the pyrimidine acts as a donor which donates two H atoms to carboxylate O atoms (acceptor). In addition, a dimeric interaction through centre of inverted symmetry related salts *via* a hydrogen bond N4—H4A···N1 (Fig. 2) forms an eight membered ring. The dihedral angle between the rings, 4-chlorophenyl and 2,4-diaminopyrimidine is 63.8 (1)°. This value is higher than that in a biphenyl ring system. This may be due to the substitution of ethyl and amine groups at C4 and C6, respectively. An extended moiety of propanamido group is slightly deviating from the plane of benzoate moiety and the dihedral angle between these two is 10.8 (1)° (Cremer & Pople, 1975; Nardelli, 1995).

The packing diagram of the molecule viewed down *b*-axis is shown in Fig. 3. Two symmetry related molecules of salt form the dimer and organize as a sheet. This sheet like dimers are connected through the hydrogen bonds N4—H4B···O3 & N2—H2A···O3 interactions. In addition, a six membered ring is formed by an intra-molecular interaction (N5—H5···O2)in benzoate molecule which also controls the molecules in crystal packing. Molecular packing is stabilized by many N—H···O and N—H···N types intra and intermolecular interactions (Table 1, Fig. 2).

S2. Experimental

A hot methanolic solution (20 ml) of 2,4-diamino-5-(4-chlorophenyl)-6- ethylpyrimidine and 2-(propanoylamino)benzoic acid in the ratio of 1:1 was warmed for 0.5 h over a water bath. The mixture was cooled slowly and kept at room temperature and after a few days, colourless crystals were obtained

S3. Refinement

H atoms were positioned geometrically and refined using a riding model with C—H = 0.93 Å for aromatic H, 0.97 Å for methylene, 0.96 Å for methyl H atoms and for aromatic NH_2 and N—H = 0.86 Å. The U_{iso} parameters for H atoms were constrained to be $1.5U_{eq}$ of the carrier atom for the methyl H atoms and $1.2U_{eq}$ of the carrier atom for the remaining H atoms.

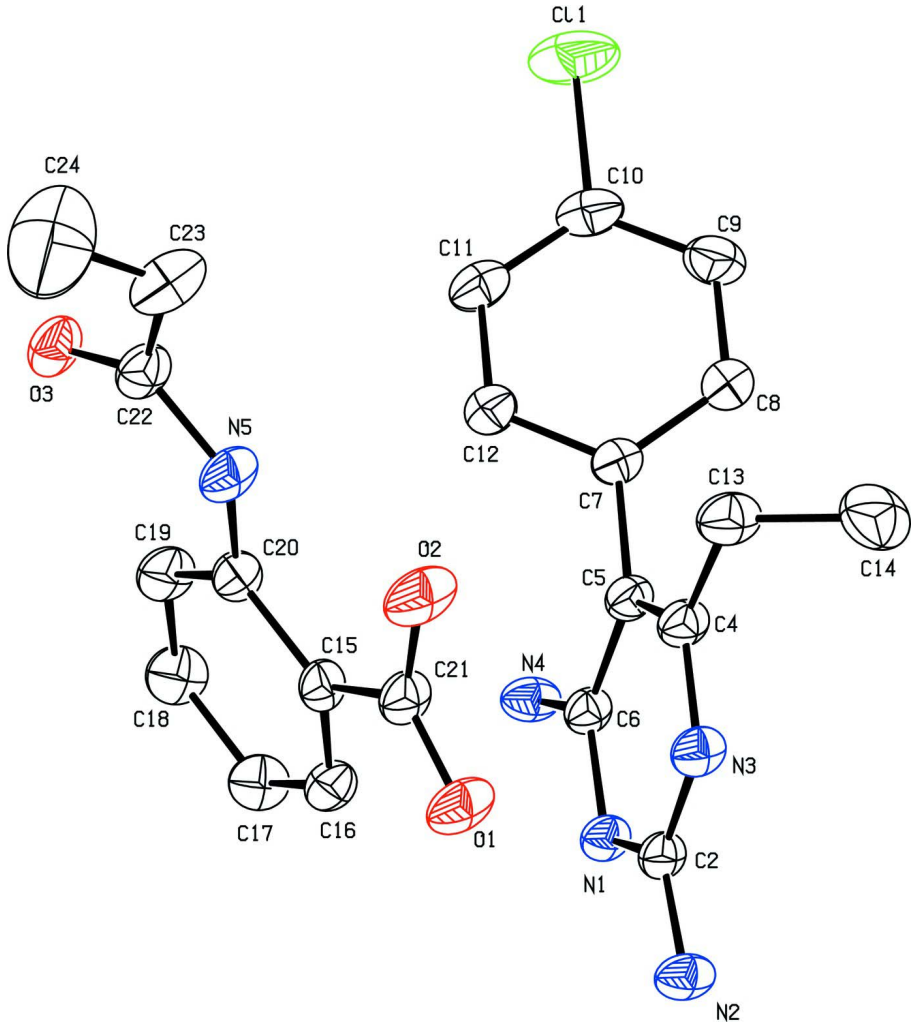

Figure 1

ORTEP diagram of the title molecule with the atom numbering scheme. Displacement ellipsoid are drawn at 30% probability level.

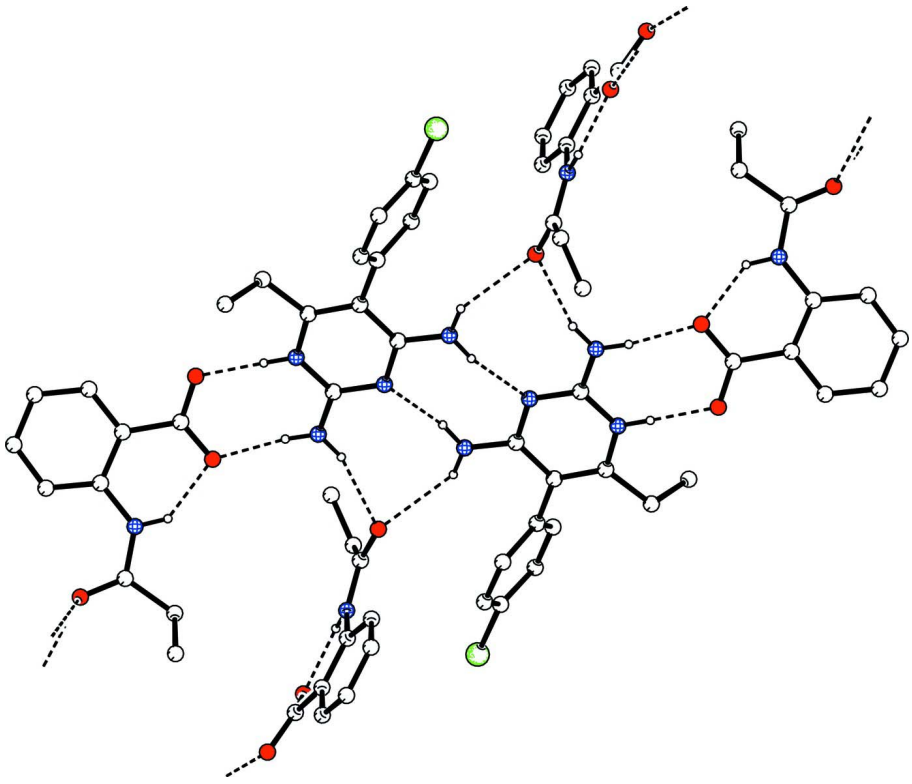

Figure 2

Dimer interaction between the symmetry related salts of title compound. Dashed lines indicate the intra and intermolecular hydrogen bonds.

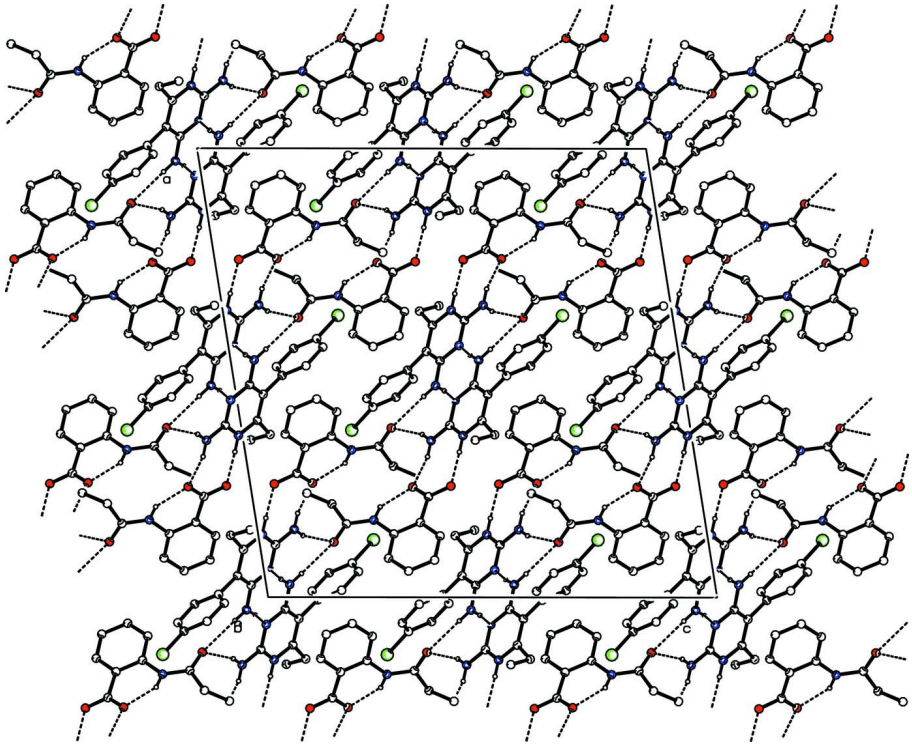

Figure 3

Packing diagram of the title compound viewed down the *b*-axis. Dashed lines indicate the intra and intermolecular interactions between the molecules.

2,4-Diamino-5-(4-chlorophenyl)-6-ethylpyrimidin-1-ium 2-propanamidobenzoate

Crystal data

$C_{12}H_{14}ClN_4^+ \cdot C_{10}H_{10}NO_3^-$
$M_r = 441.91$
Monoclinic, *C*2/*c*
$a = 22.144\ (3)$ Å
$b = 9.4915\ (14)$ Å
$c = 21.844\ (3)$ Å
$\beta = 99.071\ (3)°$
$V = 4533.7\ (12)$ Å^3
$Z = 8$
$F(000) = 1856$
$D_x = 1.295$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 17933 reflections
$\theta = 1.9–28.0°$
$\mu = 0.20$ mm^{-1}
$T = 293$ K
Block, colorless
0.50 × 0.45 × 0.42 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
17933 measured reflections
5077 independent reflections
2719 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 28.0°$, $\theta_{min} = 1.9°$
$h = -28 \rightarrow 29$
$k = -10 \rightarrow 12$
$l = -28 \rightarrow 28$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.088$
$wR(F^2) = 0.228$
$S = 1.06$
5077 reflections
281 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1005P)^2 + 1.940P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness 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 threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.62790 (7)	−0.12826 (18)	0.25493 (7)	0.1465 (7)
O1	0.25218 (12)	0.3854 (3)	0.05381 (12)	0.0926 (9)
O2	0.25430 (14)	0.2607 (4)	0.13892 (13)	0.1067 (11)
O3	0.37717 (11)	0.3960 (3)	0.33389 (11)	0.0809 (7)
N1	0.43891 (11)	0.3633 (3)	−0.01402 (11)	0.0567 (7)
N2	0.34901 (13)	0.3749 (3)	−0.08192 (12)	0.0708 (8)
H2A	0.3626	0.4469	−0.0994	0.085*
H2B	0.3130	0.3430	−0.0953	0.085*
N3	0.36043 (12)	0.2008 (3)	−0.00894 (12)	0.0640 (7)
H3	0.3237	0.1738	−0.0228	0.077*
N4	0.52835 (12)	0.3481 (3)	0.05255 (12)	0.0654 (7)
H4A	0.5399	0.4220	0.0348	0.078*
H4B	0.5525	0.3093	0.0825	0.078*
N5	0.32811 (13)	0.3417 (3)	0.23743 (12)	0.0763 (9)
H5	0.2990	0.2900	0.2188	0.092*
C2	0.38321 (14)	0.3137 (3)	−0.03469 (14)	0.0567 (8)
C4	0.39373 (15)	0.1283 (4)	0.03825 (14)	0.0620 (9)
C5	0.45211 (14)	0.1711 (3)	0.06071 (13)	0.0562 (8)
C6	0.47322 (14)	0.2937 (3)	0.03366 (13)	0.0544 (8)
C7	0.49398 (15)	0.0933 (4)	0.10941 (14)	0.0590 (8)
C8	0.51370 (18)	−0.0416 (4)	0.09988 (16)	0.0780 (10)
H8	0.4995	−0.0873	0.0627	0.094*
C9	0.5542 (2)	−0.1100 (4)	0.1447 (2)	0.0925 (13)
H9	0.5666	−0.2014	0.1378	0.111*
C10	0.57609 (18)	−0.0431 (5)	0.19934 (18)	0.0828 (11)

C11	0.55717 (17)	0.0894 (5)	0.21009 (16)	0.0770 (11)
H11	0.5722	0.1341	0.2473	0.092*
C12	0.51563 (16)	0.1586 (4)	0.16609 (15)	0.0676 (9)
H12	0.5021	0.2484	0.1742	0.081*
C13	0.36238 (19)	0.0048 (4)	0.06172 (18)	0.0857 (12)
H13A	0.3875	−0.0302	0.0990	0.103*
H13B	0.3238	0.0360	0.0729	0.103*
C14	0.3503 (3)	−0.1118 (5)	0.0168 (3)	0.1222 (18)
H14A	0.3300	−0.1870	0.0348	0.183*
H14B	0.3883	−0.1455	0.0064	0.183*
H14C	0.3247	−0.0788	−0.0200	0.183*
C15	0.33329 (14)	0.4293 (4)	0.13458 (15)	0.0596 (8)
C16	0.36330 (15)	0.5078 (4)	0.09550 (16)	0.0663 (9)
H16	0.3467	0.5132	0.0537	0.080*
C17	0.41712 (16)	0.5788 (4)	0.11626 (18)	0.0754 (10)
H17	0.4364	0.6313	0.0891	0.090*
C18	0.44141 (17)	0.5700 (4)	0.17795 (19)	0.0833 (11)
H18	0.4777	0.6169	0.1927	0.100*
C19	0.41304 (16)	0.4932 (4)	0.21807 (18)	0.0774 (10)
H19	0.4303	0.4888	0.2597	0.093*
C20	0.35892 (15)	0.4216 (4)	0.19784 (15)	0.0620 (8)
C21	0.27569 (16)	0.3551 (4)	0.10749 (16)	0.0687 (9)
C22	0.33649 (17)	0.3327 (4)	0.29967 (16)	0.0758 (10)
C23	0.2921 (2)	0.2325 (7)	0.3252 (2)	0.1161 (17)
H23A	0.2583	0.2126	0.2924	0.139*
H23B	0.3131	0.1442	0.3363	0.139*
C24	0.2684 (5)	0.2828 (11)	0.3771 (4)	0.247 (6)
H24A	0.2412	0.2139	0.3898	0.371*
H24B	0.2465	0.3689	0.3665	0.371*
H24C	0.3014	0.2999	0.4104	0.371*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.1356 (12)	0.1739 (14)	0.1179 (10)	0.0501 (10)	−0.0176 (8)	0.0603 (10)
O1	0.0793 (17)	0.122 (2)	0.0646 (15)	−0.0330 (16)	−0.0247 (13)	0.0108 (15)
O2	0.097 (2)	0.132 (3)	0.0758 (17)	−0.0575 (19)	−0.0334 (15)	0.0152 (17)
O3	0.0685 (15)	0.104 (2)	0.0626 (14)	0.0039 (14)	−0.0119 (12)	−0.0153 (14)
N1	0.0503 (14)	0.0625 (16)	0.0522 (14)	−0.0062 (13)	−0.0077 (11)	0.0027 (12)
N2	0.0611 (16)	0.0756 (19)	0.0667 (17)	−0.0151 (15)	−0.0177 (14)	0.0160 (15)
N3	0.0519 (15)	0.0730 (19)	0.0613 (16)	−0.0176 (14)	−0.0093 (12)	0.0036 (14)
N4	0.0542 (15)	0.0687 (18)	0.0675 (17)	−0.0089 (14)	−0.0082 (13)	0.0185 (14)
N5	0.0629 (17)	0.100 (2)	0.0574 (17)	−0.0223 (17)	−0.0183 (14)	−0.0015 (16)
C2	0.0562 (19)	0.0574 (19)	0.0522 (17)	−0.0120 (16)	−0.0045 (15)	−0.0012 (15)
C4	0.062 (2)	0.067 (2)	0.0534 (18)	−0.0103 (17)	−0.0020 (15)	0.0032 (16)
C5	0.0576 (18)	0.061 (2)	0.0484 (16)	−0.0032 (16)	0.0024 (14)	0.0017 (14)
C6	0.0513 (17)	0.060 (2)	0.0494 (17)	−0.0062 (16)	0.0014 (14)	−0.0001 (14)
C7	0.0579 (18)	0.065 (2)	0.0528 (18)	−0.0041 (16)	0.0051 (15)	0.0059 (15)

C8	0.098 (3)	0.072 (3)	0.061 (2)	0.006 (2)	0.005 (2)	0.0003 (18)
C9	0.116 (4)	0.078 (3)	0.085 (3)	0.033 (3)	0.020 (3)	0.019 (2)
C10	0.075 (2)	0.104 (3)	0.068 (2)	0.014 (2)	0.005 (2)	0.026 (2)
C11	0.072 (2)	0.099 (3)	0.055 (2)	−0.005 (2)	−0.0049 (18)	0.009 (2)
C12	0.069 (2)	0.073 (2)	0.058 (2)	0.0008 (18)	0.0028 (17)	0.0016 (17)
C13	0.081 (3)	0.089 (3)	0.080 (2)	−0.021 (2)	−0.009 (2)	0.016 (2)
C14	0.132 (4)	0.085 (3)	0.139 (4)	−0.026 (3)	−0.013 (4)	0.007 (3)
C15	0.0490 (17)	0.063 (2)	0.0607 (19)	0.0016 (16)	−0.0089 (15)	−0.0106 (16)
C16	0.061 (2)	0.076 (2)	0.0568 (18)	−0.0003 (18)	−0.0051 (16)	−0.0004 (17)
C17	0.055 (2)	0.084 (3)	0.084 (3)	−0.0058 (19)	0.0027 (18)	0.006 (2)
C18	0.061 (2)	0.090 (3)	0.091 (3)	−0.017 (2)	−0.013 (2)	0.002 (2)
C19	0.065 (2)	0.086 (3)	0.071 (2)	−0.012 (2)	−0.0202 (18)	0.000 (2)
C20	0.0519 (18)	0.066 (2)	0.0625 (19)	−0.0002 (17)	−0.0091 (15)	−0.0040 (17)
C21	0.062 (2)	0.078 (2)	0.060 (2)	−0.0134 (19)	−0.0081 (17)	−0.0059 (19)
C22	0.065 (2)	0.095 (3)	0.061 (2)	0.008 (2)	−0.0099 (18)	−0.005 (2)
C23	0.100 (3)	0.174 (5)	0.073 (3)	−0.012 (3)	0.009 (2)	0.015 (3)
C24	0.312 (13)	0.252 (10)	0.206 (9)	−0.147 (10)	0.126 (9)	−0.044 (8)

Geometric parameters (Å, º)

Cl1—C10	1.734 (4)	C10—C11	1.357 (6)
O1—C21	1.240 (4)	C11—C12	1.387 (5)
O2—C21	1.265 (4)	C11—H11	0.9300
O3—C22	1.232 (4)	C12—H12	0.9300
N1—C2	1.331 (4)	C13—C14	1.475 (6)
N1—C6	1.360 (4)	C13—H13A	0.9700
N2—C2	1.315 (4)	C13—H13B	0.9700
N2—H2A	0.8600	C14—H14A	0.9600
N2—H2B	0.8600	C14—H14B	0.9600
N3—C2	1.345 (4)	C14—H14C	0.9600
N3—C4	1.356 (4)	C15—C16	1.380 (5)
N3—H3	0.8600	C15—C20	1.410 (4)
N4—C6	1.330 (4)	C15—C21	1.495 (5)
N4—H4A	0.8600	C16—C17	1.382 (5)
N4—H4B	0.8600	C16—H16	0.9300
N5—C22	1.346 (4)	C17—C18	1.372 (5)
N5—C20	1.405 (4)	C17—H17	0.9300
N5—H5	0.8600	C18—C19	1.366 (5)
C4—C5	1.370 (4)	C18—H18	0.9300
C4—C13	1.494 (5)	C19—C20	1.388 (5)
C5—C6	1.417 (4)	C19—H19	0.9300
C5—C7	1.492 (4)	C22—C23	1.534 (6)
C7—C8	1.379 (5)	C23—C24	1.406 (9)
C7—C12	1.400 (4)	C23—H23A	0.9700
C8—C9	1.381 (5)	C23—H23B	0.9700
C8—H8	0.9300	C24—H24A	0.9600
C9—C10	1.372 (6)	C24—H24B	0.9600
C9—H9	0.9300	C24—H24C	0.9600

C2—N1—C6	117.6 (3)	C14—C13—H13B	108.8
C2—N2—H2A	120.0	C4—C13—H13B	108.8
C2—N2—H2B	120.0	H13A—C13—H13B	107.7
H2A—N2—H2B	120.0	C13—C14—H14A	109.5
C2—N3—C4	121.8 (3)	C13—C14—H14B	109.5
C2—N3—H3	119.1	H14A—C14—H14B	109.5
C4—N3—H3	119.1	C13—C14—H14C	109.5
C6—N4—H4A	120.0	H14A—C14—H14C	109.5
C6—N4—H4B	120.0	H14B—C14—H14C	109.5
H4A—N4—H4B	120.0	C16—C15—C20	118.4 (3)
C22—N5—C20	130.8 (3)	C16—C15—C21	118.3 (3)
C22—N5—H5	114.6	C20—C15—C21	123.4 (3)
C20—N5—H5	114.6	C15—C16—C17	122.3 (3)
N2—C2—N1	119.9 (3)	C15—C16—H16	118.8
N2—C2—N3	118.2 (3)	C17—C16—H16	118.8
N1—C2—N3	121.9 (3)	C18—C17—C16	118.5 (4)
N3—C4—C5	119.4 (3)	C18—C17—H17	120.8
N3—C4—C13	115.6 (3)	C16—C17—H17	120.8
C5—C4—C13	125.0 (3)	C19—C18—C17	120.9 (3)
C4—C5—C6	116.6 (3)	C19—C18—H18	119.5
C4—C5—C7	123.6 (3)	C17—C18—H18	119.5
C6—C5—C7	119.7 (3)	C18—C19—C20	121.2 (3)
N4—C6—N1	115.1 (3)	C18—C19—H19	119.4
N4—C6—C5	122.4 (3)	C20—C19—H19	119.4
N1—C6—C5	122.5 (3)	C19—C20—N5	123.1 (3)
C8—C7—C12	118.2 (3)	C19—C20—C15	118.7 (3)
C8—C7—C5	121.9 (3)	N5—C20—C15	118.1 (3)
C12—C7—C5	119.9 (3)	O1—C21—O2	122.7 (3)
C7—C8—C9	121.0 (4)	O1—C21—C15	118.0 (3)
C7—C8—H8	119.5	O2—C21—C15	119.2 (3)
C9—C8—H8	119.5	O3—C22—N5	123.6 (4)
C10—C9—C8	120.0 (4)	O3—C22—C23	122.0 (3)
C10—C9—H9	120.0	N5—C22—C23	114.4 (3)
C8—C9—H9	120.0	C24—C23—C22	115.1 (6)
C11—C10—C9	120.2 (4)	C24—C23—H23A	108.5
C11—C10—Cl1	120.0 (3)	C22—C23—H23A	108.5
C9—C10—Cl1	119.9 (4)	C24—C23—H23B	108.5
C10—C11—C12	120.5 (4)	C22—C23—H23B	108.5
C10—C11—H11	119.7	H23A—C23—H23B	107.5
C12—C11—H11	119.7	C23—C24—H24A	109.5
C11—C12—C7	120.0 (4)	C23—C24—H24B	109.5
C11—C12—H12	120.0	H24A—C24—H24B	109.5
C7—C12—H12	120.0	C23—C24—H24C	109.5
C14—C13—C4	114.0 (4)	H24A—C24—H24C	109.5
C14—C13—H13A	108.8	H24B—C24—H24C	109.5
C4—C13—H13A	108.8		

C6—N1—C2—N2	−178.0 (3)	C10—C11—C12—C7	−1.6 (5)
C6—N1—C2—N3	1.5 (5)	C8—C7—C12—C11	1.9 (5)
C4—N3—C2—N2	177.3 (3)	C5—C7—C12—C11	−176.4 (3)
C4—N3—C2—N1	−2.2 (5)	N3—C4—C13—C14	67.1 (5)
C2—N3—C4—C5	0.3 (5)	C5—C4—C13—C14	−112.8 (4)
C2—N3—C4—C13	−179.6 (3)	C20—C15—C16—C17	−0.1 (5)
N3—C4—C5—C6	2.0 (5)	C21—C15—C16—C17	−179.3 (3)
C13—C4—C5—C6	−178.1 (3)	C15—C16—C17—C18	0.2 (6)
N3—C4—C5—C7	−175.7 (3)	C16—C17—C18—C19	−0.2 (6)
C13—C4—C5—C7	4.2 (5)	C17—C18—C19—C20	0.1 (6)
C2—N1—C6—N4	−179.8 (3)	C18—C19—C20—N5	−179.8 (3)
C2—N1—C6—C5	1.0 (4)	C18—C19—C20—C15	0.0 (6)
C4—C5—C6—N4	178.1 (3)	C22—N5—C20—C19	10.9 (6)
C7—C5—C6—N4	−4.1 (5)	C22—N5—C20—C15	−168.9 (4)
C4—C5—C6—N1	−2.7 (5)	C16—C15—C20—C19	0.0 (5)
C7—C5—C6—N1	175.0 (3)	C21—C15—C20—C19	179.2 (3)
C4—C5—C7—C8	63.2 (5)	C16—C15—C20—N5	179.9 (3)
C6—C5—C7—C8	−114.4 (4)	C21—C15—C20—N5	−1.0 (5)
C4—C5—C7—C12	−118.5 (4)	C16—C15—C21—O1	−11.5 (5)
C6—C5—C7—C12	63.9 (4)	C20—C15—C21—O1	169.3 (3)
C12—C7—C8—C9	−0.7 (5)	C16—C15—C21—O2	165.7 (3)
C5—C7—C8—C9	177.6 (3)	C20—C15—C21—O2	−13.5 (5)
C7—C8—C9—C10	−0.9 (6)	C20—N5—C22—O3	−2.3 (6)
C8—C9—C10—C11	1.3 (6)	C20—N5—C22—C23	179.6 (4)
C8—C9—C10—Cl1	−178.9 (3)	O3—C22—C23—C24	44.3 (8)
C9—C10—C11—C12	−0.1 (6)	N5—C22—C23—C24	−137.5 (7)
Cl1—C10—C11—C12	−179.8 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5···O2	0.86	1.89	2.605 (4)	140
N2—H2*A*···O3^{i}	0.86	2.15	2.977 (4)	163
N4—H4*A*···N1^{ii}	0.86	2.16	2.988 (4)	163
N3—H3···O1^{iii}	0.86	1.80	2.660 (4)	178
C14—H14*C*···O1^{iii}	0.96	2.53	3.323 (6)	140
N2—H2*B*···O2^{iii}	0.86	1.91	2.746 (4)	164
N4—H4*B*···O3^{iv}	0.86	2.35	3.017 (3)	134

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