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Hydrogen-bonding patterns in pyrimethaminium 3,5-dinitrobenzoate

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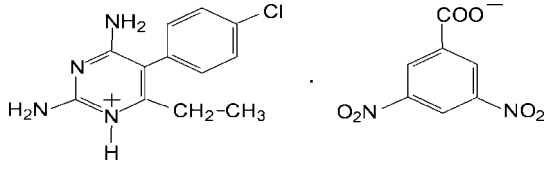
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.049; wR factor = 0.144; data-to-parameter ratio = 13.5.

In the crystal structure of the title compound [systematic name: 2,4-diamino-5-(4-chlorophenyl)-6-ethylpyrimidin-1-ium 3,5-dinitrobenzoate], $C_{12}H_{14}ClN_4^+\cdot C_7H_3N_2O_6^-$, the pyrimethamine molecule is protonated at one of the pyrimidine N atoms. The carboxylate group of the 3,5-dinitrobenzoate anion forms double hydrogen bonds of type N—H···O, resulting in a fork-like interaction with the protonated diaminopyrimidine rings [graph-set notation $R_2^2(8)$]. This motif self-assembles through a *DDAA* array of quadruple hydrogen bonds. The crystal structure is also stabilized by C—H···O hydrogen bonds.

Related literature

For related literature, see: Baskar *et al.* (2002); Cody (1984); De *et al.* (1989); Devi *et al.* (2006); Giuseppetti *et al.* (1984); Hitchings & Burchall (1965); Lynch & Jones (2004); Sansom *et al.* (1989); Sethuraman & Muthiah (2002); Sethuraman *et al.* (2003); Stanley *et al.* (2002, 2005); Taylor & Kennard (1982).



Experimental

Crystal data

$C_{12}H_{14}ClN_4^+\cdot C_7H_3N_2O_6^-$
M_r = 460.84
Monoclinic, $P2_1/c$
a = 13.034 (2) Å
b = 7.099 (2) Å
c = 22.468 (3) Å
β = 97.11 (3)°
V = 2062.9 (7) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 2.10 mm^{-1}
T = 293 K
0.13 × 0.10 × 0.08 mm

Data collection

Siemens AED single-crystal diffractometer
Absorption correction: none
4017 measured reflections
3922 independent reflections
2350 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
1 standard reflection
every 100 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.144
S = 0.91
3922 reflections
291 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 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
N1—H1···O1	0.86	1.82	2.678 (3)	176
N2—H2A···O2^{i}	0.86	2.02	2.822 (3)	156
N2—H2B···O2	0.86	1.95	2.806 (3)	172
N4—H4A···O3^{i}	0.86	2.16	3.009 (4)	170
C7—H7B···O6^{ii}	0.97	2.60	3.331 (4)	133
C11—H11···O5^{iii}	0.93	2.49	3.252 (4)	139
C13—H13···O4^{iv}	0.93	2.55	3.455 (4)	165

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

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; 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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LW2025).

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supplementary materials

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Hydrogen-bonding patterns in pyrimethaminium 3,5-dinitrobenzoate

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Comment

Pyrimethamine [PMN] is an well known antifolate drug used in the treatment of malaria. In the chemotheraphy of malaria and neoplastic diseases, substituted 2,4-diaminopyrimidines are widely employed as metabolic inhibitors of pathways leading to the synthesis of proteins and nucleic acid (Hitchings & Burchall, 1965). The crystal structures of PMN (Sethuraman & Muthiah, 2002) and some of its complexes such as PMN hydrogen succinate, PMN hydrogen maleate, PMN hydrogen phthalate and PMN fumarate (Sethuraman *et al.*, 2003), and PMN hydrogen glutarate and PMN formate (Stanley *et al.*, 2002) have been reported from our laboratory. Most of the supramolecular crystals originate from strong N—H···O and O—H···N hydrogen bonds; the weak C—H···O bonds are known to play a significant role in determining the molecular packing of organic solids (Taylor & Kennard,1982). The present study has been undertaken to study the hydrogen bonding patterns involved in aminopyrimidine-carboxylate interactions.

The asymmetric unit of (I) contains a protonated PMN cation and a 3,5-dintrobenzoate anion. PMN is protonated at N1, as evident from the increase in the internal angle at N1 from 116.25 (18)° in neutral PMN molecule A and 116.09 (18)° in molecule B (Sethuraman & Muthiah, 2002) to 121.5 (2)°. The key conformational features of the PMN cations are described by two angles. The first is the dihedral angle between the 2,4-diaminopyrimidine and the 4-chlorophenyl mean planes. The second is the torsion angle that represents the deviation of the ethyl group from the pyrimidine plane. The dihedral angle between the pyrimidine and benzene ring is 63.17 (13)° and the torsion angle C5—C6—C7—C8 is −100.3 (3)°. These values are close to those observed in modelling studies of dihydrofolate reductase-pyrimethamine complexes, which indicates that these angles play an important role in the proper docking of the drug molecule in the active site of the enzyme (Sansom *et al.*, 1989). The bond connecting the pyrimidine ring and the C5—C9 benzene ring is 1.490 (4)Å in length (De *et al.*, 1989). The PMN cation interacts with atoms O1 and O2 of the carboxylate group, forming a cyclic hydrogen-bonded $R_2^2(8)$ dimer (Lynch & Jones, 2004). Two such motifs, related by inversion, are hydrogen-bonded to give a complementary DDAA (D= donor in hydrogen bond, A=acceptor in hydrogen bond) array of quadruple hydrogen-bonding patterns, comprising fused $R_2^2(8)$, $R_4^2(8)$ and $R_2^2(8)$ motifs (Fig. 2). A similar type of interaction has been observed in pyrimethaminium 3-chlorobenzoate (Devi *et al.*, 2006), PMN nitrobenzoate salts (Stanley *et al.*, 2005) and in some TMP(trimethoprim) salts with oxy acids (Giuseppetti *et al.*, 1984; Cody, 1984; Baskar Raj *et al.*, 2002). Each DDAA array is flanked on either side by $R_2^2(14)$ ring through N—H···O hydrogen bonds involving 4-amino group and one of the oxygen (O3) atom of the 5-nitro group. Here, one of the hydrogen (H7B) atom of the methylene ($-CH_2$) group interacts with O6 oxygen atom of the 6-nitro group through C—H···O hydrogen bonds. Two inversion related PMN cations (atoms C11 and C13) and 3,5-dinitro benzoate anions (O5 & O6) are connected through the weak C—H···O hydrogen bonds forming a 24 membered ring with graph-set notation $R_4^4(24)$ as shown in Fig. 3.

Experimental

A hot methanol solution of pyrimethamine (62 mg, Shah Pharma Chemicals., India) and an aqueous solution of 3,5-dinitrobenzoic acid (53 mg, Merck) were mixed in a 1:1 molar ratio and warmed for half an hour over a water bath. The product was then recrystallized from ethanol. After about a week, colourless crystals of (I) were obtained.

Refinement

Methyl H atoms were placed in idealized positions, with U_{iso}(H)= 1.5Ueq(C). Other H atoms were placed in idealized positions, with C—H =0.97 (methylene) and 0.93Å (aromatic), and N—H = 0.86 Å, and refined as riding on their carrier atoms, with U_{iso}(H) = 1.2Ueq (C, N).

Figures

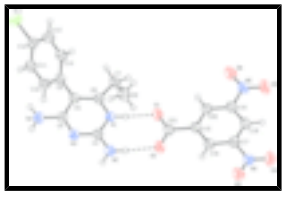


Fig. 1. An *ORTEP* view of the asymmetric unit of (I) showing 50% probability displacement ellipsoids.

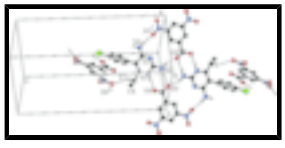


Fig. 2. Hydrogen bonding patterns in compound (I). Symmetry codes: (i) −*x*, −*y*, −*z*; (ii) −*x*, *y* − 1/2, −*z* + 1/2.

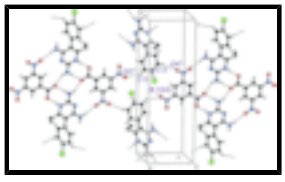


Fig. 3. A view of C—H···O interactions in compound (I). Symmetry codes: (iii) −*x*, *y* − 3/2, −*z* + 1/2; (iv) 1 + *x*, −*y* + 3/2, 1/2 + *z*.

2,4-diamino-5-(4-chlorophenyl)-6-ethylpyrimidin-1-ium 3,5-dinitrobenzoate

Crystal data

$C_{12}H_{14}ClN_4^+ \cdot C_7H_3N_2O_6^-$	F_{000} = 952
M_r = 460.84	D_x = 1.484 Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation λ = 1.54178 Å
Hall symbol: -P 2ybc	Cell parameters from 45 reflections
a = 13.034 (2) Å	θ = 3.4–70.2°
b = 7.099 (2) Å	μ = 2.10 mm^{-1}
c = 22.468 (3) Å	*T* = 293 K
β = 97.11 (3)°	Prism, colourless
V = 2062.9 (7) Å^3	0.13 × 0.10 × 0.08 mm
Z = 4	

Data collection

Siemens AED single-crystal diffractometer	R_{int} = 0.022
Radiation source: fine-focus sealed tube	θ_{max} = 70.2º
Monochromator: graphite	θ_{min} = 3.4º
T = 293 K	h = −15→14
ω–2θ scans	k = −8→8
Absorption correction: none	l = −8→27
4017 measured reflections	1 standard reflections
3922 independent reflections	every 100 reflections
2350 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.049	$w = 1/[\sigma^2(F_o^2) + (0.0787P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.144	$(\Delta/\sigma)_{max} < 0.001$
S = 0.91	$\Delta\rho_{max}$ = 0.23 e Å^{-3}
3922 reflections	$\Delta\rho_{min}$ = −0.24 e Å^{-3}
291 parameters	Extinction correction: SHELXL97, $FC^*=KFC[1+0.001XFC^2\Lambda^3/SIN(2\Theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0010 (2)
Secondary atom site location: difference Fourier map	

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	0.52577 (7)	0.23938 (13)	0.45621 (4)	0.0715 (3)
N1	0.10982 (16)	0.1850 (3)	0.15156 (9)	0.0413 (7)
N2	0.06617 (19)	−0.0094 (3)	0.07126 (10)	0.0534 (8)

N3	0.19609 (18)	−0.1033 (3)	0.14335 (10)	0.0464 (7)
N4	0.3256 (2)	−0.1913 (4)	0.21484 (12)	0.0613 (9)
C2	0.1242 (2)	0.0225 (4)	0.12227 (12)	0.0408 (8)
C4	0.2526 (2)	−0.0642 (4)	0.19524 (12)	0.0427 (8)
C5	0.2411 (2)	0.1036 (4)	0.22933 (12)	0.0414 (8)
C6	0.1659 (2)	0.2262 (4)	0.20558 (11)	0.0400 (8)
C7	0.1334 (2)	0.4014 (4)	0.23515 (13)	0.0479 (9)
C8	0.0348 (3)	0.3676 (5)	0.26294 (16)	0.0669 (12)
C9	0.3088 (2)	0.1389 (4)	0.28669 (12)	0.0427 (8)
C10	0.3087 (2)	0.0216 (4)	0.33584 (12)	0.0478 (9)
C11	0.3758 (2)	0.0503 (4)	0.38781 (13)	0.0526 (10)
C12	0.4418 (2)	0.2014 (4)	0.39072 (13)	0.0486 (9)
C13	0.4434 (2)	0.3226 (5)	0.34340 (14)	0.0571 (10)
C14	0.3783 (2)	0.2898 (4)	0.29103 (13)	0.0530 (10)
O1	−0.02513 (18)	0.4454 (3)	0.10443 (9)	0.0642 (8)
O2	−0.06964 (17)	0.2731 (3)	0.02248 (9)	0.0610 (7)
O3	−0.3249 (2)	0.5328 (3)	−0.13549 (10)	0.0716 (9)
O4	−0.4092 (2)	0.7804 (4)	−0.11937 (11)	0.0882 (10)
O5	−0.3036 (2)	1.1559 (4)	0.05664 (12)	0.0925 (10)
O6	−0.1869 (2)	1.0551 (3)	0.12436 (10)	0.0747 (9)
N5	−0.3424 (2)	0.6653 (3)	−0.10412 (11)	0.0524 (8)
N6	−0.2407 (2)	1.0385 (3)	0.07634 (11)	0.0565 (9)
C15	−0.1492 (2)	0.5704 (4)	0.02909 (12)	0.0419 (8)
C16	−0.2084 (2)	0.5473 (4)	−0.02585 (12)	0.0447 (8)
C17	−0.2784 (2)	0.6882 (4)	−0.04601 (12)	0.0434 (8)
C18	−0.2896 (2)	0.8512 (4)	−0.01397 (13)	0.0472 (9)
C19	−0.2291 (2)	0.8697 (4)	0.03992 (12)	0.0449 (9)
C20	−0.1582 (2)	0.7329 (4)	0.06244 (12)	0.0447 (9)
C21	−0.0745 (2)	0.4170 (4)	0.05396 (13)	0.0465 (9)
H1	0.06440	0.26430	0.13590	0.0500*
H2A	0.07450	−0.11090	0.05150	0.0640*
H2B	0.01990	0.07110	0.05760	0.0640*
H4A	0.33350	−0.29080	0.19400	0.0740*
H4B	0.36440	−0.17310	0.24820	0.0740*
H7A	0.12230	0.50170	0.20570	0.0580*
H7B	0.18780	0.44070	0.26600	0.0580*
H8A	−0.02020	0.33660	0.23200	0.1000*
H8B	0.01700	0.47950	0.28340	0.1000*
H8C	0.04510	0.26540	0.29100	0.1000*
H10	0.26250	−0.07880	0.33390	0.0570*
H11	0.37610	−0.03150	0.42020	0.0630*
H13	0.48770	0.42570	0.34650	0.0690*
H14	0.38070	0.36910	0.25830	0.0640*
H16	−0.20160	0.44010	−0.04880	0.0540*
H18	−0.33620	0.94450	−0.02840	0.0570*
H20	−0.11770	0.75000	0.09910	0.0540*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0730 (5)	0.0757 (6)	0.0580 (5)	−0.0147 (4)	−0.0234 (4)	0.0001 (4)
N1	0.0449 (12)	0.0360 (11)	0.0410 (12)	0.0058 (10)	−0.0025 (10)	−0.0030 (9)
N2	0.0620 (15)	0.0468 (13)	0.0472 (14)	0.0135 (12)	−0.0102 (11)	−0.0143 (11)
N3	0.0486 (13)	0.0410 (12)	0.0474 (13)	0.0063 (10)	−0.0030 (10)	−0.0056 (10)
N4	0.0671 (17)	0.0504 (14)	0.0602 (16)	0.0203 (13)	−0.0167 (13)	−0.0138 (12)
C2	0.0446 (15)	0.0371 (13)	0.0395 (14)	0.0022 (11)	−0.0001 (11)	−0.0038 (11)
C4	0.0438 (15)	0.0361 (13)	0.0470 (15)	0.0040 (11)	0.0007 (12)	−0.0021 (12)
C5	0.0466 (15)	0.0348 (13)	0.0418 (15)	0.0002 (11)	0.0010 (12)	−0.0011 (11)
C6	0.0458 (14)	0.0331 (13)	0.0400 (14)	−0.0011 (11)	0.0011 (11)	−0.0020 (11)
C7	0.0567 (17)	0.0392 (14)	0.0453 (16)	0.0036 (13)	−0.0042 (13)	−0.0081 (12)
C8	0.076 (2)	0.060 (2)	0.066 (2)	0.0129 (17)	0.0143 (18)	−0.0121 (17)
C9	0.0477 (16)	0.0355 (13)	0.0435 (15)	0.0019 (11)	0.0006 (12)	−0.0024 (12)
C10	0.0515 (16)	0.0379 (14)	0.0523 (17)	−0.0101 (12)	−0.0005 (13)	0.0029 (13)
C11	0.0633 (19)	0.0452 (16)	0.0465 (16)	−0.0074 (14)	−0.0039 (14)	0.0047 (13)
C12	0.0464 (15)	0.0517 (17)	0.0444 (15)	−0.0011 (13)	−0.0078 (12)	−0.0056 (13)
C13	0.0598 (19)	0.0485 (16)	0.0604 (19)	−0.0151 (14)	−0.0029 (15)	0.0018 (15)
C14	0.0619 (19)	0.0443 (16)	0.0505 (17)	−0.0084 (14)	−0.0024 (14)	0.0097 (13)
O1	0.0791 (15)	0.0488 (12)	0.0572 (13)	0.0225 (11)	−0.0212 (11)	−0.0088 (10)
O2	0.0760 (14)	0.0493 (12)	0.0528 (12)	0.0239 (11)	−0.0115 (10)	−0.0122 (10)
O3	0.0985 (18)	0.0525 (13)	0.0577 (13)	0.0149 (13)	−0.0142 (12)	−0.0140 (11)
O4	0.0986 (19)	0.0760 (17)	0.0780 (17)	0.0400 (15)	−0.0369 (14)	−0.0123 (14)
O5	0.117 (2)	0.0597 (15)	0.0901 (18)	0.0453 (15)	−0.0292 (16)	−0.0253 (14)
O6	0.115 (2)	0.0535 (13)	0.0500 (13)	0.0183 (13)	−0.0120 (13)	−0.0116 (11)
N5	0.0606 (15)	0.0433 (13)	0.0504 (14)	0.0029 (12)	−0.0051 (12)	0.0007 (12)
N6	0.0746 (18)	0.0415 (13)	0.0516 (15)	0.0112 (13)	0.0004 (13)	−0.0069 (12)
C15	0.0460 (15)	0.0345 (13)	0.0449 (15)	0.0052 (11)	0.0042 (12)	0.0009 (11)
C16	0.0517 (16)	0.0368 (13)	0.0454 (15)	0.0049 (12)	0.0054 (12)	−0.0009 (12)
C17	0.0490 (15)	0.0398 (14)	0.0395 (14)	0.0005 (12)	−0.0022 (12)	0.0023 (12)
C18	0.0551 (17)	0.0360 (14)	0.0497 (16)	0.0086 (12)	0.0034 (13)	0.0014 (12)
C19	0.0575 (17)	0.0322 (13)	0.0448 (15)	0.0042 (12)	0.0054 (13)	−0.0007 (12)
C20	0.0519 (16)	0.0378 (14)	0.0429 (15)	0.0022 (12)	0.0002 (12)	−0.0001 (12)
C21	0.0494 (16)	0.0416 (15)	0.0468 (16)	0.0094 (12)	−0.0006 (13)	0.0006 (13)

Geometric parameters (Å, °)

Cl1—C12	1.743 (3)	C9—C10	1.383 (4)
O1—C21	1.249 (4)	C9—C14	1.398 (4)
O2—C21	1.249 (4)	C10—C11	1.385 (4)
O3—N5	1.214 (3)	C11—C12	1.371 (4)
O4—N5	1.212 (4)	C12—C13	1.370 (4)
O5—N6	1.214 (4)	C13—C14	1.383 (4)
O6—N6	1.218 (3)	C7—H7A	0.9706
N1—C2	1.353 (4)	C7—H7B	0.9692
N1—C6	1.369 (3)	C8—H8B	0.9605
N2—C2	1.312 (4)	C8—H8C	0.9596

N3—C4	1.329 (4)	C8—H8A	0.9603
N3—C2	1.338 (4)	C10—H10	0.9306
N4—C4	1.345 (4)	C11—H11	0.9307
N1—H1	0.8600	C13—H13	0.9295
N2—H2B	0.8595	C14—H14	0.9297
N2—H2A	0.8602	C15—C16	1.382 (4)
N4—H4A	0.8606	C15—C20	1.388 (4)
N4—H4B	0.8605	C15—C21	1.520 (4)
N5—C17	1.469 (4)	C16—C17	1.391 (4)
N6—C19	1.469 (4)	C17—C18	1.380 (4)
C4—C5	1.434 (4)	C18—C19	1.367 (4)
C5—C6	1.369 (4)	C19—C20	1.392 (4)
C5—C9	1.490 (4)	C16—H16	0.9296
C6—C7	1.496 (4)	C18—H18	0.9295
C7—C8	1.516 (5)	C20—H20	0.9296
Cl1···C18^{i}	3.575 (3)	C19···C11^{viii}	3.493 (4)
Cl1···O5^{ii}	3.057 (3)	C20···C11^{viii}	3.429 (4)
Cl1···H18^{ii}	2.8703	C20···N2^{x}	3.434 (4)
O1···N1	2.678 (3)	C20···C10^{viii}	3.526 (4)
O1···C7	3.390 (4)	C21···C21^{iv}	3.494 (4)
O2···N2^{iii}	2.822 (3)	C2···H8B^{i}	2.9896
O2···C15^{iv}	3.396 (4)	C6···H14	3.0740
O2···N2	2.806 (3)	C6···H8B^{i}	2.9929
O2···N6^{v}	3.143 (3)	C8···H1	3.0177
O3···N4^{iii}	3.009 (4)	C8···H8B^{i}	2.9927
O3···C6^{iv}	3.242 (4)	C9···H7B	2.6669
O5···Cl1^{vi}	3.057 (3)	C9···H4B	2.5167
O5···C11^{vii}	3.252 (4)	C10···H4B	2.5824
O6···C7^{viii}	3.331 (4)	C14···H7B	2.6988
O6···C8^{viii}	3.297 (4)	C21···H1	2.6490
O1···H1	1.8194	C21···H2B	2.7432
O1···H20	2.4719	H1···O2	2.9065
O1···H7A	2.8191	H1···H2B	2.2494
O2···H1	2.9065	H1···C8	3.0177
O2···H16	2.4993	H1···C21	2.6490
O2···H2A^{iii}	2.0166	H1···O1	1.8194
O2···H2B	1.9527	H1···H8A	2.5944
O3···H16	2.4566	H1···H7A	2.3614
O3···H4A^{iii}	2.1577	H2A···O2^{iii}	2.0166
O3···H14^{iv}	2.8515	H2B···O2	1.9527
O4···H13^{vi}	2.5479	H2B···H1	2.2494
O4···H18	2.4410	H2B···C21	2.7432
O5···H18	2.4254	H4A···O3^{iii}	2.1577
O5···H11^{vii}	2.4920	H4B···H10	2.5598

O6···H7B^{viii}	2.5952	H4B···C10	2.5824
O6···H20	2.4400	H4B···C9	2.5167
O6···H8B^{viii}	2.8898	H7A···H1	2.3614
N1···O1	2.678 (3)	H7A···O1	2.8191
N2···O2^{iii}	2.822 (3)	H7B···C14	2.6988
N2···C20^{v}	3.434 (4)	H7B···H14	2.5918
N2···O2	2.806 (3)	H7B···O6^{i}	2.5952
N4···C13^{ix}	3.430 (4)	H7B···C9	2.6669
N4···O3^{iii}	3.009 (4)	H8A···N1	2.8381
N4···C10	3.142 (4)	H8A···H1	2.5944
N6···O2^{x}	3.143 (3)	H8A···H8B^{i}	2.5596
N1···H8B^{i}	2.7557	H8B···N1^{viii}	2.7557
N1···H8A	2.8381	H8B···C8^{viii}	2.9927
C2···C18^{iv}	3.560 (4)	H8B···C2^{viii}	2.9896
C2···C17^{iv}	3.471 (4)	H8B···C6^{viii}	2.9929
C6···O3^{iv}	3.242 (4)	H8B···O6^{i}	2.8898
C7···C14	3.377 (4)	H8B···H8A^{viii}	2.5596
C7···O1	3.390 (4)	H8C···H20^{i}	2.5350
C7···O6^{i}	3.331 (4)	H10···H4B	2.5598
C8···O6^{i}	3.297 (4)	H11···O5^{xi}	2.4920
C10···C20^{i}	3.526 (4)	H13···O4^{ii}	2.5479
C10···N4	3.142 (4)	H14···H7B	2.5918
C11···C20^{i}	3.429 (4)	H14···O3^{iv}	2.8515
C11···O5^{xi}	3.252 (4)	H14···C6	3.0740
C11···C19^{i}	3.493 (4)	H16···O2	2.4993
C12···C19^{i}	3.551 (4)	H16···O3	2.4566
C13···N4^{xii}	3.430 (4)	H18···O4	2.4410
C14···C7	3.377 (4)	H18···O5	2.4254
C15···O2^{iv}	3.396 (4)	H18···Cl1^{vi}	2.8703
C17···C2^{iv}	3.471 (4)	H20···O1	2.4719
C18···C2^{iv}	3.560 (4)	H20···O6	2.4400
C18···Cl1^{viii}	3.575 (3)	H20···H8C^{viii}	2.5350
C19···C12^{viii}	3.551 (4)		
C2—N1—C6	121.5 (2)	C6—C7—H7A	109.49
C2—N3—C4	117.3 (2)	C6—C7—H7B	109.55
C2—N1—H1	119.28	C8—C7—H7A	109.54
C6—N1—H1	119.21	H7A—C7—H7B	108.09
C2—N2—H2A	119.96	H8B—C8—H8C	109.47
C2—N2—H2B	120.01	C7—C8—H8B	109.48
H2A—N2—H2B	120.03	C7—C8—H8A	109.46
H4A—N4—H4B	120.01	H8A—C8—H8C	109.48
C4—N4—H4A	119.99	C7—C8—H8C	109.48
C4—N4—H4B	120.00	H8A—C8—H8B	109.46

O3—N5—O4	122.6 (3)	C9—C10—H10	119.22
O3—N5—C17	118.4 (2)	C11—C10—H10	119.32
O4—N5—C17	119.1 (2)	C12—C11—H11	120.59
O5—N6—O6	123.1 (3)	C10—C11—H11	120.58
O6—N6—C19	119.0 (2)	C12—C13—H13	120.36
O5—N6—C19	117.9 (2)	C14—C13—H13	120.43
N1—C2—N3	122.0 (2)	C13—C14—H14	119.60
N2—C2—N3	119.8 (3)	C9—C14—H14	119.58
N1—C2—N2	118.2 (2)	C16—C15—C20	120.4 (3)
N3—C4—C5	124.0 (2)	C16—C15—C21	120.3 (3)
N3—C4—N4	116.1 (3)	C20—C15—C21	119.3 (2)
N4—C4—C5	119.9 (2)	C15—C16—C17	118.5 (3)
C6—C5—C9	123.3 (3)	N5—C17—C16	119.2 (2)
C4—C5—C6	115.9 (2)	N5—C17—C18	118.1 (2)
C4—C5—C9	120.8 (2)	C16—C17—C18	122.7 (3)
C5—C6—C7	125.7 (2)	C17—C18—C19	117.1 (3)
N1—C6—C7	115.0 (2)	N6—C19—C18	118.9 (2)
N1—C6—C5	119.2 (2)	N6—C19—C20	118.4 (2)
C6—C7—C8	110.6 (2)	C18—C19—C20	122.6 (3)
C10—C9—C14	118.0 (3)	C15—C20—C19	118.7 (2)
C5—C9—C10	122.0 (2)	O1—C21—O2	126.1 (3)
C5—C9—C14	119.9 (2)	O1—C21—C15	116.9 (3)
C9—C10—C11	121.5 (3)	O2—C21—C15	116.9 (2)
C10—C11—C12	118.8 (3)	C15—C16—H16	120.76
Cl1—C12—C11	119.1 (2)	C17—C16—H16	120.77
Cl1—C12—C13	119.3 (2)	C17—C18—H18	121.49
C11—C12—C13	121.6 (3)	C19—C18—H18	121.39
C12—C13—C14	119.2 (3)	C15—C20—H20	120.67
C9—C14—C13	120.8 (3)	C19—C20—H20	120.64
C8—C7—H7B	109.48		
C6—N1—C2—N2	178.6 (2)	N1—C6—C7—C8	76.1 (3)
C6—N1—C2—N3	−2.3 (4)	C5—C6—C7—C8	−100.3 (3)
C2—N1—C6—C5	2.6 (4)	C14—C9—C10—C11	−0.6 (4)
C2—N1—C6—C7	−174.0 (2)	C5—C9—C14—C13	−178.6 (3)
C4—N3—C2—N1	1.1 (4)	C5—C9—C10—C11	176.6 (3)
C4—N3—C2—N2	−179.9 (3)	C10—C9—C14—C13	−1.3 (4)
C2—N3—C4—N4	−178.8 (2)	C9—C10—C11—C12	1.6 (4)
C2—N3—C4—C5	−0.2 (4)	C10—C11—C12—C13	−0.6 (4)
O4—N5—C17—C18	−6.9 (4)	C10—C11—C12—Cl1	179.5 (2)
O3—N5—C17—C16	−7.2 (4)	C11—C12—C13—C14	−1.2 (4)
O3—N5—C17—C18	171.9 (3)	Cl1—C12—C13—C14	178.6 (2)
O4—N5—C17—C16	174.0 (3)	C12—C13—C14—C9	2.2 (4)
O6—N6—C19—C18	180.0 (3)	C20—C15—C16—C17	−1.5 (4)
O6—N6—C19—C20	1.3 (4)	C21—C15—C16—C17	177.8 (2)
O5—N6—C19—C20	−179.1 (3)	C16—C15—C20—C19	1.1 (4)
O5—N6—C19—C18	−0.5 (4)	C21—C15—C20—C19	−178.1 (2)
N4—C4—C5—C9	−0.4 (4)	C16—C15—C21—O1	−178.5 (3)
N3—C4—C5—C9	−178.9 (3)	C16—C15—C21—O2	0.3 (4)
N4—C4—C5—C6	179.1 (3)	C20—C15—C21—O1	0.8 (4)

N3—C4—C5—C6	0.6 (4)	C20—C15—C21—O2	179.6 (3)
C4—C5—C9—C10	−62.7 (4)	C15—C16—C17—N5	−179.6 (2)
C4—C5—C6—C7	174.5 (3)	C15—C16—C17—C18	1.3 (4)
C9—C5—C6—N1	177.7 (2)	N5—C17—C18—C19	−179.9 (2)
C4—C5—C9—C14	114.5 (3)	C16—C17—C18—C19	−0.7 (4)
C6—C5—C9—C10	117.9 (3)	C17—C18—C19—N6	−178.2 (2)
C4—C5—C6—N1	−1.7 (4)	C17—C18—C19—C20	0.4 (4)
C6—C5—C9—C14	−64.9 (4)	N6—C19—C20—C15	178.0 (2)
C9—C5—C6—C7	−6.0 (4)	C18—C19—C20—C15	−0.6 (4)

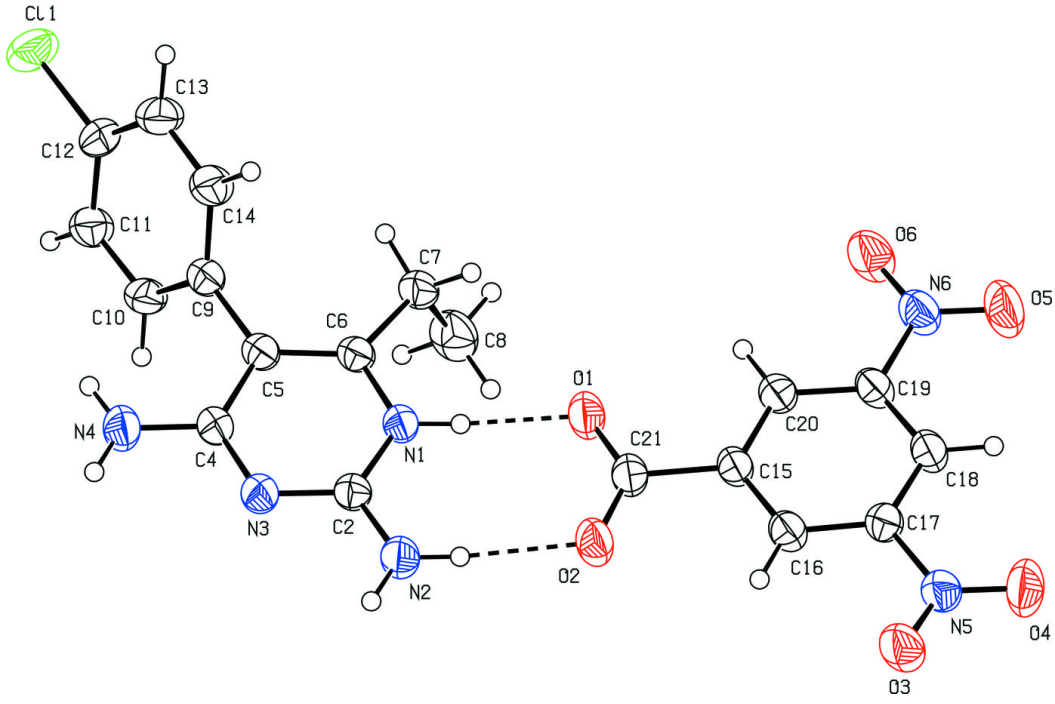
Symmetry codes: (i) −*x*, *y*−1/2, −*z*+1/2; (ii) *x*+1, −*y*+3/2, *z*+1/2; (iii) −*x*, −*y*, −*z*; (iv) −*x*, −*y*+1, −*z*; (v) *x*, *y*−1, *z*; (vi) *x*−1, −*y*+3/2, *z*−1/2; (vii) −*x*, *y*+3/2, −*z*+1/2; (viii) −*x*, *y*+1/2, −*z*+1/2; (ix) −*x*+1, *y*−1/2, −*z*+1/2; (x) *x*, *y*+1, *z*; (xi) −*x*, *y*−3/2, −*z*+1/2; (xii) −*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···O1	0.86	1.82	2.678 (3)	176
N2—H2A···O2^{iii}	0.86	2.02	2.822 (3)	156
N2—H2B···O2	0.86	1.95	2.806 (3)	172
N4—H4A···O3^{iii}	0.86	2.16	3.009 (4)	170
C7—H7B···O6^{i}	0.97	2.60	3.331 (4)	133
C11—H11···O5^{xi}	0.93	2.49	3.252 (4)	139
C13—H13···O4^{ii}	0.93	2.55	3.455 (4)	165

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

Fig. 1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N4
C4
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C20
C19
O6
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O5
C15
C18
N3
C2
C17
C16
N2
O2
N5
O4
O3

Fig. 2

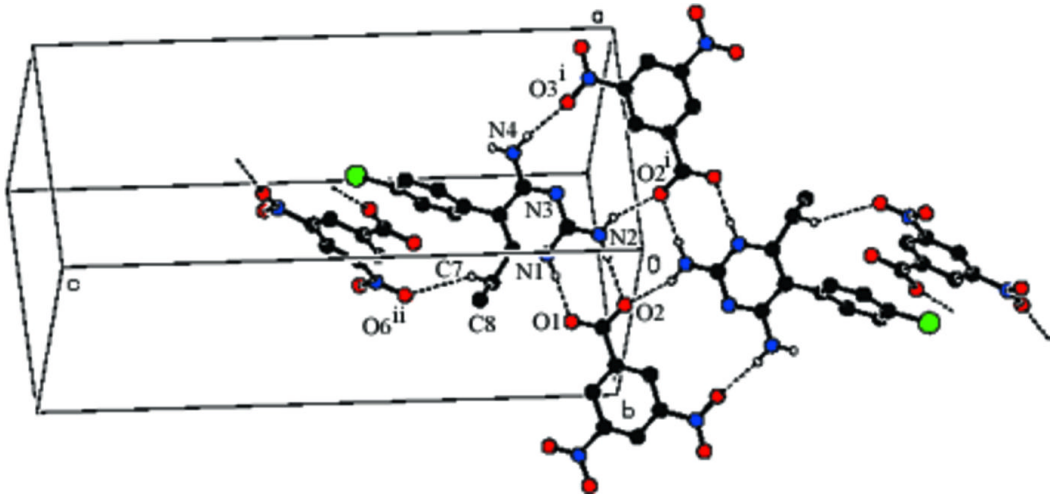

Fig. 3