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Hydrogen-bonding patterns in 2-amino-4,6-dimethylpyrimidinium picrate

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Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.060
wR factor = 0.201
Data-to-parameter ratio = 11.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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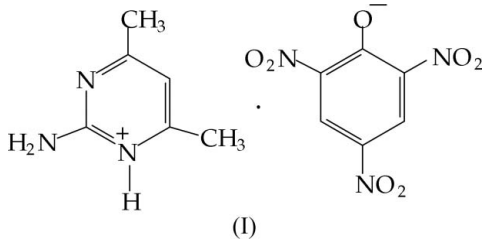
In the title structure, $C_6H_{10}N_3^+\cdot C_6H_2N_3O_7^-$, the asymmetric unit consists of a 2-amino-4,6-dimethylpyrimidinium cation and a picrate (2,4,6-trinitrophenolate) anion. In the crystal structure, inversion-symmetry-related cations are paired *via* N—H···N hydrogen bonds, whereas inversion-related anions are paired *via* weak C—H···O hydrogen bonds. The cations and anions further interact with each other through N—H···O hydrogen bonds.

Comment

It is known that picric acid functions not only as an acceptor to form π-stacking complexes with aromatic biomolecules, but also as an acidic ligand to form salts with polar biomolecules through specific electrostatic or hydrogen-bonding interactions (In *et al.*, 1997). Pyrimidine and aminopyrimidine derivatives are biologically important compounds as they occur in nature as components of nucleic acids. Some aminopyrimidine derivatives are used as antifolate drugs (Hunt *et al.*, 1980; Baker & Santi, 1965). The crystal structure of 2-amino-4,6-dimethyl pyrimidinium bromide 2-amino-4,6-dimethyl pyrimidine monohydrate (Panneerselvam *et al.*, 2004) has already been reported from our laboratory. Most supramolecular crystals originate from strong N—H···O and O—H···N hydrogen bonds, but weak C—H···O bonds are known to play a significant role in determining the molecular packing of organic solids (Taylor & Kennard, 1982).



(I)

The asymmetric unit of (I) (Fig.1) contains one 2-amino-4,6-dimethylpyrimidinium cation and a picrate anion. Protonation of the aminopyrimidine base on position N1 is reflected in the C2—N1—C6 angle compared with the C2—N3—C4 angle at unprotonated atom N3 (Table 1). In the crystal structure, inversion-related aminopyrimidine cations are paired *via* N—H···N hydrogen bonds (Table 2), generating a motif with graph-set notation $R_2^2(8)$ (Bernstein *et al.*, 1995). This motif is flanked on either side by an $R_3^2(8)$ ring involving N—H···N and C—H···O hydrogen bonds, leading to the formation of a fused $R_3^2(8)$, $R_2^2(8)$ and $R_3^2(8)$ ring sequence. The cation further interacts with the picrate ion *via* N—H···O hydrogen bonds

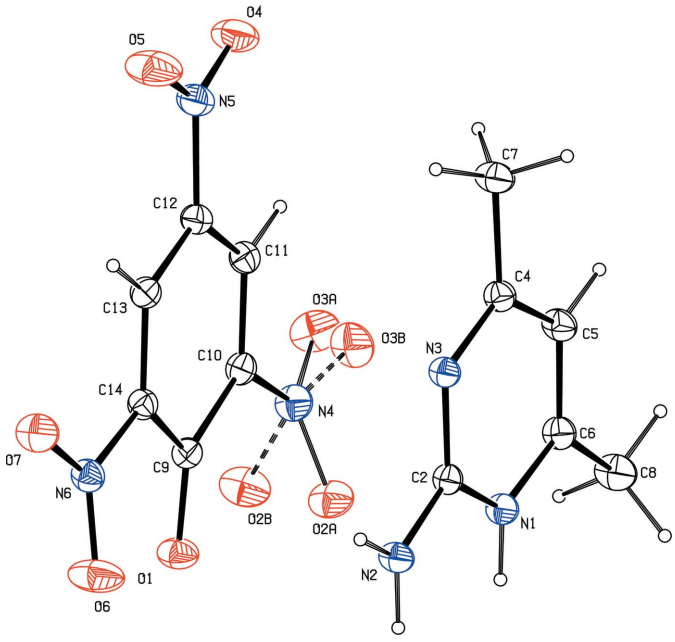


Figure 1
The asymmetric unit of (I) showing 30% probability displacement ellipsoids. Both components of the disordered atoms are shown.

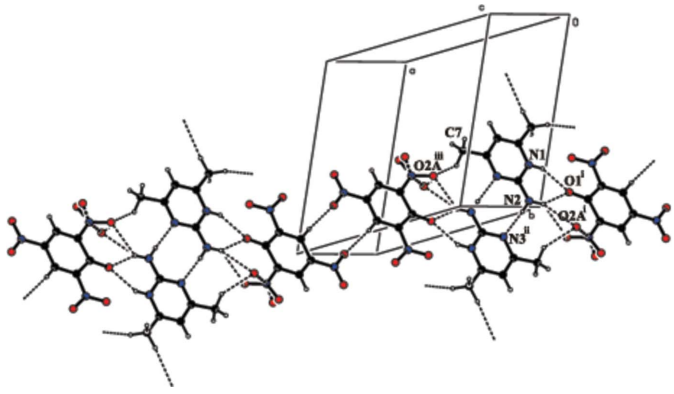


Figure 2
Part of the crystal structure of (I) showing hydrogen bonds as dashed lines [symmetry codes: (i) $-x, 2-y, -z$; (ii) $-x, 2-y, 1-z$; (iii) $x, y, 1+z$]. Both disorder components are shown.

forming an $R_2^1(6)$ ring, with the phenolate O atom acting as a bifurcated acceptor and the amino H atom acting as a hydrogen-bond donor. Two inversion-related picrate ions are paired *via* a pair of C—H···O(nitro) interactions forming an $R_2^2(10)$ ring (Fig. 2). The combination of all types of intermolecular hydrogen bonds forms a three-dimensional network (Table 2 and Fig. 3). In addition, there are significant π–π stacking interactions (Hunter, 1994). In the crystal structure, picrate anions and pyrimidine rings have a perpendicular separation of 3.495 Å, a centroid-to-centroid distance of 3.799 (2) Å and a slip angle (the angle between the centroid vector and the normal to the plane) of 27.5°. Stacking interactions are also observed between the picrate anions with a perpendicular separation of 3.336 Å, a centroid-to-centroid distance of 3.545 (2) Å and a slip angle of 19.78°.

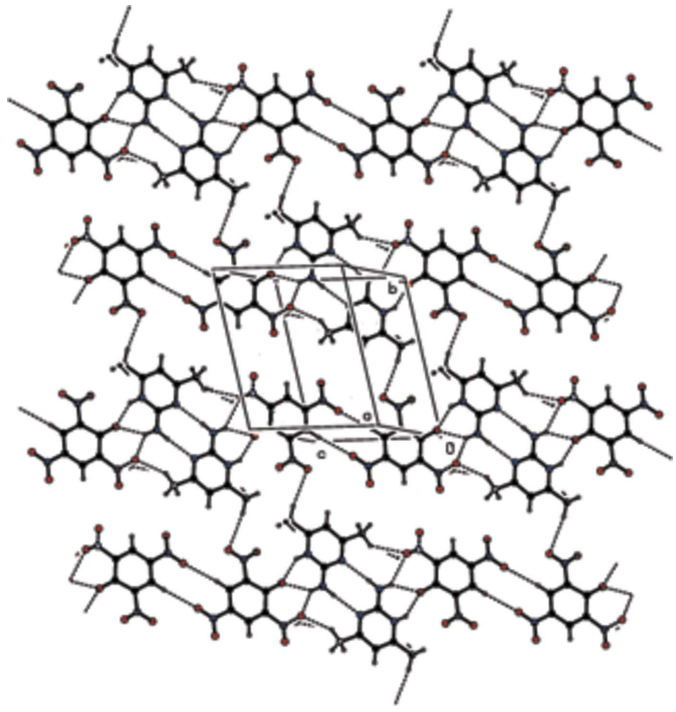


Figure 3
A view of the hydrogen-bonded (dashed lines) three-dimensional network in (I).

Experimental

Hot ethanol solutions of 2-amino-4,6-dimethyl pyrimidine (31 mg) and picric acid (57 mg) were mixed in equimolar ratio. The solution was warmed over a water bath for half an hour and kept at room temperature for crystallization. Total evaporation of the solvent gave yellow prisms of (I).

Crystal data

$C_6H_{10}N_3^+\cdot C_6H_2N_3O_7^-$
M_r = 352.28
Triclinic, $P\overline{1}$
a = 9.646 (3) Å
b = 10.990 (3) Å
c = 8.351 (3) Å
α = 79.86 (3)°
β = 67.75 (3)°
γ = 66.62 (3)°
V = 751.7 (5) Å^3
Z = 2
D_x = 1.556 Mg m^{-3}
Cu $K\alpha$ radiation
μ = 1.13 mm^{-1}
T = 153 K
Prism, yellow
0.17 × 0.14 × 0.10 mm

Data collection

Siemens AED single-crystal diffractometer
ω–2θ scans
Absorption correction: none
2841 measured reflections
2841 independent reflections
1974 reflections with $I > 2\sigma(I)$
R_{int} = 0.000
θ_{max} = 69.9°
1 standard reflections
every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.201
S = 1.01
2841 reflections
247 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1398P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C9	1.242 (3)	N4—C10	1.456 (3)
O2*A*—N4	1.235 (7)	N5—C12	1.449 (4)
O2*B*—N4	1.311 (10)	N6—C14	1.452 (3)
O3*A*—N4	1.237 (10)	N1—C6	1.357 (3)
O3*B*—N4	1.124 (18)	N1—C2	1.361 (3)
O4—N5	1.214 (3)	N2—C2	1.322 (3)
O5—N5	1.206 (4)	N3—C4	1.334 (3)
O6—N6	1.206 (4)	N3—C2	1.342 (3)
O7—N6	1.206 (3)		
O2*A*—N4—O3*A*	122.0 (5)	O1—C9—C14	124.6 (2)
O2*A*—N4—C10	117.9 (3)	N4—C10—C9	119.2 (2)
O3*A*—N4—C10	119.1 (5)	N4—C10—C11	116.6 (2)
O2*B*—N4—C10	115.0 (5)	N5—C12—C13	119.3 (2)
O3*B*—N4—C10	120.9 (12)	N5—C12—C11	119.8 (2)
O2*B*—N4—O3*B*	121.2 (12)	N6—C14—C9	119.7 (2)
O4—N5—O5	122.4 (3)	N6—C14—C13	115.9 (2)
O4—N5—C12	118.9 (3)	N1—C2—N3	121.41 (19)
O5—N5—C12	118.7 (2)	N2—C2—N3	119.7 (2)
O6—N6—O7	121.1 (2)	N1—C2—N2	118.9 (2)
O6—N6—C14	119.6 (2)	N3—C4—C7	117.6 (2)
O7—N6—C14	119.2 (2)	N3—C4—C5	122.0 (2)
C2—N1—C6	121.5 (2)	N1—C6—C8	118.2 (3)
C2—N3—C4	117.8 (2)	N1—C6—C5	117.9 (2)
O1—C9—C10	123.9 (2)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.88	2.02	2.799 (3)	148
N2—H2*A*···N3^{ii}	0.88	2.23	3.107 (3)	176
N2—H2*B*···O1^{i}	0.88	2.06	2.837 (3)	146
N2—H2*B*···O2*A*^{i}	0.88	2.33	3.038 (5)	138
C7—H7*A*···O2*A*^{iii}	0.98	2.43	3.190 (6)	134
C8—H8*A*···O4^{iv}	0.98	2.50	3.369 (5)	147
C8—H8*B*···O7^{v}	0.98	2.58	3.539 (4)	166
C13—H13···O5^{vi}	0.95	2.55	3.497 (4)	175

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

All H atoms were located in a difference Fourier map but were relocated in idealized positions with C—H and N—H bond lengths of 0.95–0.98 and 0.88 Å, respectively. They were included in the refinement in the riding-model approximation with U_{iso}(H) = $1.2U_{eq}$(C,N), or $1.5U_{eq}$(C) for methyl H atoms. The O atoms of the 4-nitro group containing atom N4 were refined as disordered over two sites with final values of the site-occupation factors of 0.688 (8):0.312 (8) for O2*A*/O3*A*:O2*B*/O3*B*.

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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