Hydrogen-bonding and π–π interactions in 2-amino-4,6-dimethyl-pyrimidinium salicylate

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In the crystal structure of the title compound, $C_6H_{10}N_3{}^+ \cdot C_7H_5O_3{}^-$, the asymmetric unit contains four crystallographically independent 2-amino-4,6-dimethylpyrimidinium and salicylate ions ($Z = 8$). In each of these, one of the pyrimidine N atoms is protonated, and the carboxylate group of the salicylate ion interacts with the pyrimidine group through a pair of N—H···O hydrogen bonds, forming an $R_2^2(8)$ motif. The pyrimidine cations also form base pairs via a pair of N—H···N hydrogen bonds (involving the amino group and the unprotonated ring N atom), forming another $R_2^2(8)$ motif. Three such $R_2^2(8)$ motifs, fused together, constitute a closed cyclic aggregate, and the linking of these aggregates, arranged in consecutive layers, can be analysed in terms of off-face stacking interactions.

Comment

The hydrogen-bonding patterns, including base pairing, formed by aminopyrimidines, and base stacking, are important in nucleic acid structures and their functions. Some aminopyrimidine derivatives are used as antifolate drugs (Hunt *et al.*, 1980; Baker & Santi, 1965). 2-Aminopyrimidine and its derivatives are of particular interest as adduct formers because of their ability to form stable hydrogen-bonded chains via their stereochemically associated amine group and the ring N atoms (Lynch *et al.*, 2000; Lynch & Jones, 2004). Salicylic acid is a widely used analgesic. The crystal structures of aminopyrimidine derivatives (Schwalbe & Williams, 1982), aminopyrimidine carboxylates (Hu *et al.*, 2002) and cocrystal structures (Chinnakali *et al.*, 1999) have been reported. The crystal structure of 2-amino-4,6-dimethylpyrimidinium bromide 2-amino-4,6-dimethylpyrimidine monohydrate (Panneerselvam *et al.*, 2004), 2-amino-4,6-dimethylpyrimidinium hydrogen sulfate (Hemamalini *et al.*, 2005), bis(2,4-diamino-6-oxopyrimidinium) sulfate monohydrate (Muthiah *et al.*, 2004) and 2-amino-4,6-dimethylpyrimidine–cinnamic acid (1/2) (Balasubramani *et al.*, 2005) have recently been reported from our laboratory. The present study is aimed at investigating the supramolecular interactions of the title compound, (I).
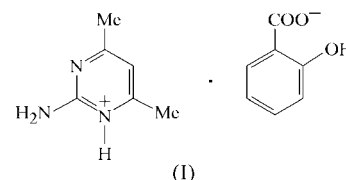
The asymmetric unit of (I) consists of four crystallographically independent 2-amino-4,6-dimethylpyrimidinium cations and salicylate anions, as shown in Fig. 1. The constituent atoms of all four ionic pairs have been labelled in an identical manner, except that the individual molecules are identified by the suffix *A*, *B*, *C* or *D*. Protonation of the pyrimidine base on the N1 site is reflected in a change in bond
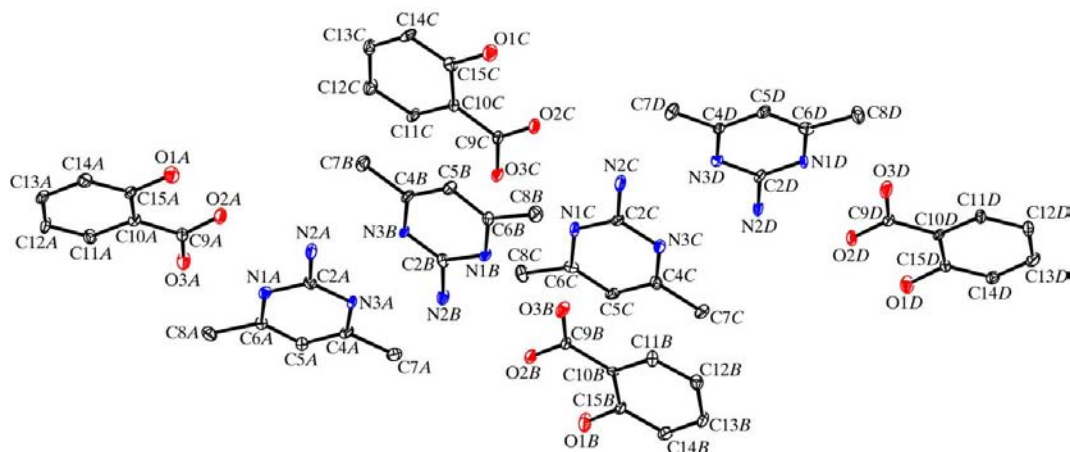

Figure 1
A molecular drawing of the asymmetric unit of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

angle compared with the unprotonated site (Panneerselvam *et al.*, 2004). The average value of the valence angle at the unprotonated atom N3 for the four molecules in the asymmetric unit is 116.7 (5)°, and that at the protonated atom N1 120.1 (5)° (Table 1). The geometry of the pyrimidine cation agrees with that of other pyrimidine cations reported in the literature (Panneerselvam *et al.*, 2004).

A view of the molecular packing of (I) is shown in Fig. 2. The constituents of each ionic pair (*A*, *B*, *C* or *D*) are bonded through a pair of N—H···O hydrogen bonds, forming an eight-membered hydrogen-bonded ring motif with graph-set $R_2^2(8)$ (Bernstein *et al.*, 1995). The independent ionic pairs pack in pairs (*A* and *B*, and *C* and *D*). Pairs of hydrogen bonds involving the 2-amino group and pyrimidine atom N3 link cation *A* to cation *B* (N2*B*—H2*B*1···N3*A* and N3*B*···H2*A*2—

N2*A*) and cation *C* to cation *D* (N2*D*—H2*D*1···N3*C* and N3*D*···H2*C*1—N2*C*), forming an $R_2^2(8)$ ring motif. The typical intramolecular hydrogen bond between the phenolic –OH and the carboxylate group is also present in all the salicylate moieties (Panneerselvam *et al.*, 2002). Hence, the eight-component asymmetric unit can be considered as being composed of two closed cyclic aggregates, each consisting of two 2-amino-4,6-dimethylpyrimidinium cations and two salicylate anions, together forming the $R_8^6(28)$ hydrogen-bond pattern. Within each aggregate, the pyrimidine cations are inclined to each other at 18.2 (3) and 17.5 (2)°, and the salicylate anions at 23.2 (3) and 25.6 (3)°. The aggregates formed by molecules *A* and *B*, and those formed by molecules *C* and *D*, lie on two adjacent parallel planes.

These aggregates are inclined to each other at an angle of 13.2 (2)°, and are linked by off-face π–π interactions. The 2-amino-4,6-dimethylpyrimidinium cation *A* forms stacking interactions with the aryl rings of the salicylate anions of molecules C^{i} and D^{ii}, with perpendicular separations of 3.292 and 3.389 Å, respectively, centroid-to-centroid distances of 3.683 (3) and 3.681 (3) Å, respectively, and slip angles (the angle between the centroid vector and the normal to the plane) of 18.6 and 16.2°, respectively [symmetry codes: (i) $-x$, $\frac{1}{2} + y$, $-z$; (ii) $x, y, -1 + z$]. A similar type of stacking is also observed between the 2-amino-4,6-dimethylpyrimidinium cations of molecules C^{i} and D^{iii} and salicylate anion *A*, with perpendicular separations of 3.295 and 3.434 Å, respectively, centroid-to-centroid distances of 3.725 (3) and 3.751 (3) Å, respectively, and slip angles of 20.27 and 19.91°, respectively (Fig. 3) [symmetry code: (iii) $x, y, 1 + z$]. These are all typical aromatic stacking values (Hunter, 1994).
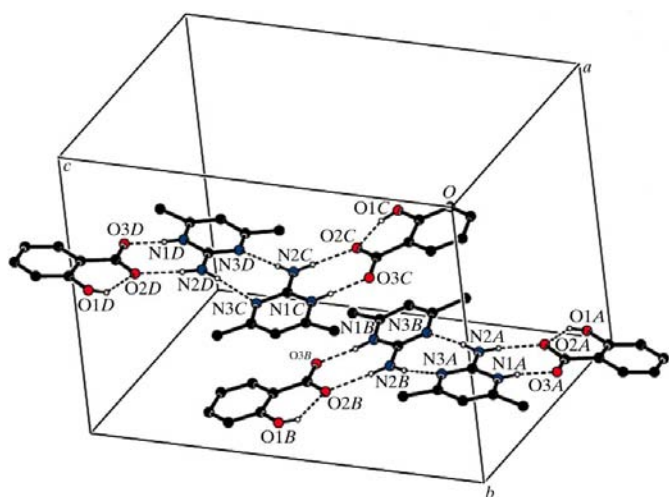

Figure 2
A view of the hydrogen-bonding interactions in (I) (dashed lines). For clarity, H atoms not involved in hydrogen bonding have been omitted.
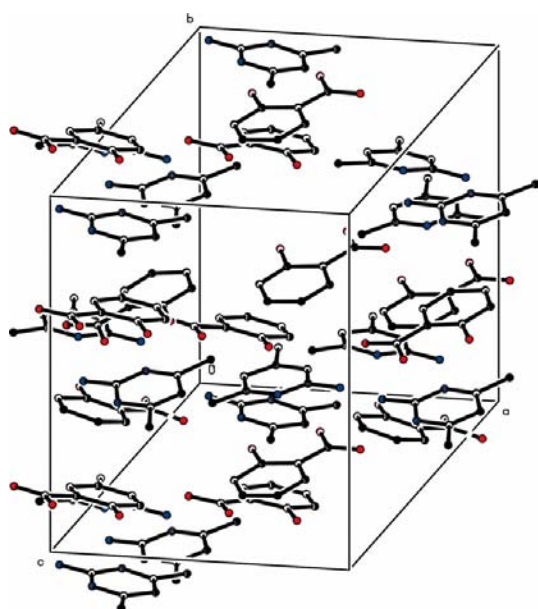
Experimental

A hot methanol solution (20 ml) of 2-amino-4,6-dimethylpyrimidine (31 mg; Aldrich) and a methanol solution (20 ml) of salicylic acid (45 mg; LOBA Chemie, India) were mixed in a 1:1 molar ratio and warmed for 30 min over a water bath. On slow evaporation of the resulting mixture, prismatic colourless crystals of (I) were obtained.

Crystal data

$C_6H_{10}N_3^+ \cdot C_7H_5O_3^-$	$Z = 8$
$M_r = 261.28$	$D_x = 1.310$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 11.039$ (2) Å	$\mu = 0.10$ mm^{-1}
$b = 13.995$ (3) Å	$T = 295$ (2) K
$c = 17.371$ (3) Å	Prismatic, colourless
$\beta = 99.04$ (3)°	$0.45 \times 0.3 \times 0.2$ mm
$V = 2650.3$ (9) Å^3	

Data collection

Kuma KM-4 CCD κ-geometry diffractometer	4865 independent reflections
	2229 reflections with $I > 2\sigma(I)$
ω scans	$R_{\mathrm{int}} = 0.082$
20586 measured reflections	$\theta_{\mathrm{max}} = 25.0°$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.045$	$w = 1/[\sigma^2(F_o^2) + (0.0195P)^2]$
$wR(F^2) = 0.082$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.90$	$(\Delta/\sigma)_{\mathrm{max}} = 0.001$
4865 reflections	$\Delta\rho_{\mathrm{max}} = 0.14$ e Å^{-3}
698 parameters	$\Delta\rho_{\mathrm{min}} = -0.12$ e Å^{-3}

Figure 3
A view of the π–π stacking interactions in compound (I). H atoms have been omitted.

Table 1
Selected geometric parameters (Å, °).

O1A—C15A	1.372 (9)	N3B—C4B	1.343 (9)
O2A—C9A	1.272 (8)	N3B—C2B	1.329 (9)
O3A—C9A	1.267 (9)	O3C—C9C	1.246 (9)
N1A—C6A	1.322 (9)	N1C—C6C	1.337 (9)
N1A—C2A	1.354 (9)	N1C—C2C	1.366 (9)
O1B—C15B	1.344 (8)	O1D—C15D	1.373 (8)
N2A—C2A	1.318 (9)	N2C—C2C	1.327 (9)
O2B—C9B	1.264 (8)	O2D—C9D	1.270 (8)
N3A—C2A	1.337 (9)	N3C—C4C	1.288 (9)
N3A—C4A	1.348 (9)	N3C—C2C	1.348 (9)
O3B—C9B	1.262 (9)	O3D—C9D	1.252 (9)
N1B—C6B	1.336 (8)	N1D—C2D	1.339 (9)
N1B—C2B	1.371 (9)	N1D—C6D	1.363 (9)
O1C—C15C	1.352 (8)	N2D—C2D	1.341 (8)
N2B—C2B	1.325 (8)	N3D—C2D	1.346 (9)
O2C—C9C	1.279 (8)	N3D—C4D	1.297 (10)
C2A—N1A—C6A	120.3 (6)	N1C—C6C—C8C	115.8 (6)
C2A—N3A—C4A	114.5 (6)	N2D—C2D—N3D	118.7 (6)
C2B—N1B—C6B	120.3 (5)	N1D—C2D—N2D	118.2 (6)
C2B—N3B—C4B	116.3 (6)	N1D—C2D—N3D	123.0 (6)
C2C—N1C—C6C	120.2 (6)	N3D—C4D—C7D	118.9 (6)
C2C—N3C—C4C	117.1 (6)	N3D—C4D—C5D	122.3 (6)
C2D—N1D—C6D	119.2 (6)	N1D—C6D—C8D	114.8 (5)
C2D—N3D—C4D	118.0 (6)	N1D—C6D—C5D	119.3 (6)
N1A—C2A—N3A	123.7 (7)	O2A—C9A—O3A	123.8 (6)
N1A—C2A—N2A	116.9 (6)	O3A—C9A—C10A	118.9 (6)
N2A—C2A—N3A	119.4 (6)	O2A—C9A—C10A	117.2 (6)
N3A—C4A—C7A	114.0 (6)	O1A—C15A—C10A	120.9 (6)
N3A—C4A—C5A	124.2 (6)	O1A—C15A—C14A	116.7 (7)
N1A—C6A—C8A	116.2 (6)	O2B—C9B—O3B	123.4 (6)
N1A—C6A—C5A	119.8 (6)	O2B—C9B—C10B	118.3 (6)
N1B—C2B—N2B	117.4 (6)	O3B—C9B—C10B	118.3 (6)
N2B—C2B—N3B	120.1 (6)	O1B—C15B—C10B	123.0 (6)
N1B—C2B—N3B	122.5 (6)	O1B—C15B—C14B	116.4 (6)
N3B—C4B—C7B	115.1 (6)	O3C—C9C—C10C	120.0 (6)
N3B—C4B—C5B	122.8 (6)	O2C—C9C—O3C	124.3 (6)
N1B—C6B—C5B	119.6 (5)	O2C—C9C—C10C	115.7 (6)
N1B—C6B—C8B	117.1 (5)	O1C—C15C—C10C	119.6 (6)
N1C—C2C—N3C	122.1 (6)	O1C—C15C—C14C	120.8 (6)
N1C—C2C—N2C	119.2 (6)	O2D—C9D—C10D	118.3 (6)
N2C—C2C—N3C	118.7 (6)	O3D—C9D—C10D	117.2 (6)
N3C—C4C—C7C	117.5 (6)	O2D—C9D—O3D	124.5 (6)
N3C—C4C—C5C	123.2 (7)	O1D—C15D—C14D	117.5 (6)
N1C—C6C—C5C	118.1 (6)	O1D—C15D—C10D	121.6 (6)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2B—H2B1···N3A	0.86	2.23	3.086 (7)	171
N1A—H1A···O3A	0.86	1.74	2.598 (7)	172
N1B—H1B···O3B	0.86	1.72	2.580 (6)	174
N1C—H1C···O3C	0.86	1.74	2.600 (7)	177
N1D—H1D···O3D	0.86	1.71	2.572 (7)	176
N2B—H2B2···O2B	0.86	2.03	2.888 (6)	178
N2D—H2D1···O2D	0.86	2.03	2.883 (6)	175
N2D—H2D2···N3C	0.86	2.16	3.021 (7)	175
O1B—H1B1···O2B	0.82	1.88	2.577 (6)	142
O1D—H1D1···O2D	0.82	1.87	2.569 (6)	143
N2A—H2A1···N3B	0.86	2.09	2.946 (7)	172
N2A—H2A2···O2A	0.86	1.99	2.847 (6)	174
N2C—H2C1···O2C	0.86	1.98	2.835 (6)	175
N2C—H2C2···N3D	0.86	2.15	3.005 (6)	177
O1A—H1A1···O2A	0.82	1.84	2.517 (6)	138
O1C—H1C1···O2C	0.82	1.78	2.510 (6)	147
C11C—H11C···O3C	0.93	2.46	2.782 (8)	100

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In the absence of significant anomalous scattering effects, Friedel pairs were averaged. All H atoms were located in difference Fourier maps and were then relocated in idealized positions and refined as riding on their carrier atoms, with N—H = 0.85–0.86 Å, O—H = 0.82 Å and C—H = 0.95–0.96 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2000); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2000); data reduction: *CrysAlis RED*; 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*.