Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Co-existence of water-mediated and normal base pairs in a supramolecular ribbon in 2-amino-4,6-dimethylpyrimidinium bromide 2-amino-4,6-dimethylpyrimidine monohydrate

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Received 23 March 2004
Accepted 30 March 2004
Online 9 April 2004

In the crystal structure of the title compound, $C_6H_{10}N_3^+ \cdot Br^- \cdot C_6H_9N_3 \cdot H_2O$, the asymmetric unit contains a 2-amino-4,6-dimethylpyrimidinium cation, a Br^- anion, a neutral 2-amino-4,6-dimethylpyrimidine molecule and a water molecule. Each neutral base molecule is paired with another inversion-related molecule through N—H···N hydrogen bonds to form dimers, and these are linked to one another through water-mediated hydrogen bonds, generating a supramolecular ribbon. The cations also pair with one another through N—H···N hydrogen bonds. The cation pairs are stacked on top of the neutral pairs. The Br^- anion also takes part in hydrogen bonding (N/O—H···Br).

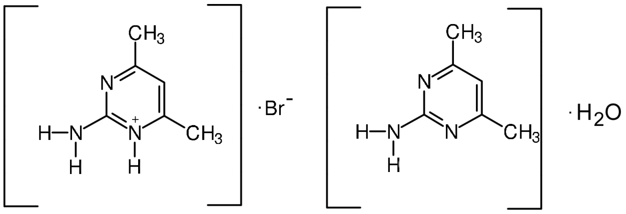
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.045
wR factor = 0.136
Data-to-parameter ratio = 15.2

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

Comment

Hydrogen-bonding patterns, including base-pairing, formed by aminopyrimidines are important in nucleic acid structures and their functions. Some aminopyrimidine derivatives are used as antifolate drugs (Hunt *et al.*, 1980; Baker & Santi, 1965). In crystal structures of aminopyrimidine derivatives (Schwalbe & Williams, 1982) and aminopyrimidinecarboxylates (Hu *et al.*, 2002), and in cocrystal structures (Chinnakali *et al.*, 1999; Goswami *et al.*, 2000; Etter *et al.*, 1990), a supramolecular ribbon motif made up of base pairs has been observed. The crystal structures are further stabilized by C—H···O hydrogen bonds bridging the supramolecular ribbons. In the present work, the crystal structure of the title compound, (I), has been investigated in order to study the hydrogen-bonded interactions.



(I)

The asymmetric unit of (I) consists of 2-amino-4,6-dimethylpyrimidine, its protonated form, a Br^- anion and a water molecule (Fig. 1). Regarding the protonated species, the protonation has occurred at one of the ring N atoms (N11), as reported in various crystal structures containing aminopyrimidine cations (Wagner & Philopsborn, 1970; Furberg & Grogaard, 1980). This is evident from an increase in the internal angle at N11, which has increased to 122.0 (4)° (C12—N11—C16), compared with 116.4 (4)° (C2—N1—C6) and

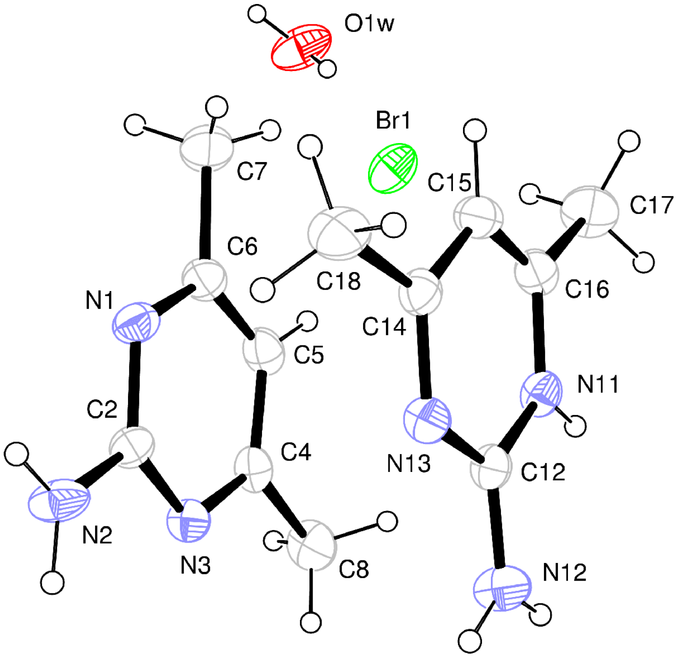


Figure 1
A view of the contents of the asymmetric unit of (I), showing 30% probability displacement ellipsoids.

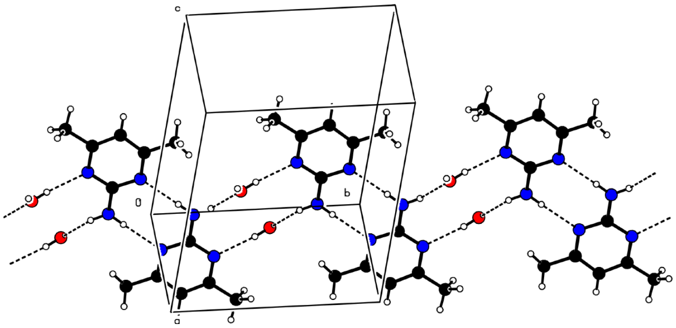


Figure 2
A view of the water-mediated base pairs in the crystal structure of (I).

116.8 (4)° (C2—N3—C4) in the neutral molecule in the same asymmetric unit. The bond lengths and angles (Table 1) agree with those reported in related crystal structures (Aoki & Yamazaki, 1985, 1989).

In the crystal structure of (I), the neutral base molecule is paired with an inversion-equivalent molecule through N2—H2*A*···N3(−*x*, −*y*, 2 − *z*) hydrogen bonds to form dimers (Table 2), and these dimers are linked to one another through water-mediated hydrogen bonds (Fig. 2). This water-mediated base pairing is an elegant example of the unique role of water in biomolecular interactions. The structural chemistry of water in biomolecules is of great interest. Water-mediated base pairs have also been observed in a few RNA structures (Holbrook *et al.*, 1991). Recently, computational studies have been carried out on water-mediated base pairs. It has also been suggested that these water-mediated base pairs may be involved in conformational switching between different conformations of nucleic acids (Schneider *et al.*, 2001).

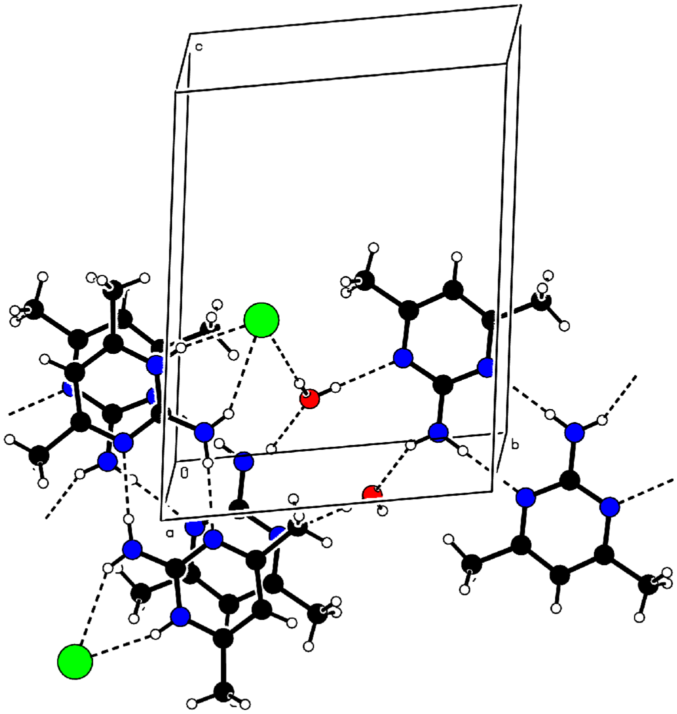


Figure 3
A view of the stacked pairs in (I).

The cations in (I) are also paired with one another through N12—H12*A*···N13(1 − *x*, −*y*, 2 − *z*) hydrogen bonds. The cations are stacked on top of the neutral base molecules (Fig. 3), with their centroids alternately separated by 3.492 (4) and 3.530 (4) Å. The corresponding slip angles (between the plane normal and the line joining the centroids) are 14.6 and 15.2°, respectively. The amino group and pyrimidine N atom interact with the Br$^-$ anion *via* N12—H12*B*···Br1(1 − *x*, −*y*, 1 − *z*) and N11—H11···Br1(1 − *x*, −*y*, 1 − *z*) hydrogen bonds, to form a six-membered hydrogen-bonded ring. In addition, O1*W*—H1*A*···Br1 hydrogen bonds also stabilize the crystal structure.

Experimental

To an aqueous methanol solution of 2-amino-4,6-dimethylpyrimidine (62 mg, Aldrich), a few drops of dilute hydrobromic acid were added. The solution was warmed over a water bath for a few minutes. The resulting solution was allowed to cool slowly to room temperature and allowed to stand. Colourless crystals of (I) were obtained after a few days.

Crystal data

$C_6H_{10}N_3^+ \cdot Br^- \cdot C_6H_9N_3 \cdot H_2O$
$M_r = 345.25$
Triclinic, $P\overline{1}$
$a = 7.002$ (4) Å
$b = 9.438$ (8) Å
$c = 12.658$ (6) Å
$\alpha = 79.56$ (5)°
$\beta = 83.85$ (4)°
$\gamma = 82.98$ (6)°
$V = 813.4$ (9) Å^3

$Z = 2$
$D_x = 1.410$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 3$–25°
$\mu = 2.53$ mm^{-1}
$T = 293$ K
Block, colourless
0.35 × 0.35 × 0.25 mm

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Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.439$, $T_{\max} = 0.531$
3101 measured reflections
2843 independent reflections
2095 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.030$
$\theta_{\max} = 25.0^\circ$
$h = 0 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = -14 \rightarrow 15$
2 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.136$
$S = 1.14$
2843 reflections
187 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0646P)^2 + 0.8382P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.47$ e Å^{-3}
$\Delta\rho_{\min} = -0.57$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N11—C16	1.351 (6)	N1—C6	1.338 (6)
N11—C12	1.354 (5)	N1—C2	1.353 (5)
N12—C12	1.320 (5)	N2—C2	1.334 (5)
N13—C12	1.339 (5)	N3—C4	1.327 (5)
N13—C14	1.331 (6)	N3—C2	1.346 (5)
C12—N11—C16	122.0 (4)	N11—C16—C17	116.4 (4)
C12—N13—C14	117.2 (4)	N11—C16—C15	117.3 (4)
C2—N1—C6	116.4 (4)	N1—C2—N3	125.3 (4)
C2—N3—C4	116.8 (4)	N2—C2—N3	117.2 (4)
N12—C12—N13	119.6 (4)	N1—C2—N2	117.5 (4)
N11—C12—N13	121.6 (4)	N3—C4—C5	121.7 (4)
N11—C12—N12	118.8 (4)	N3—C4—C8	117.0 (4)
N13—C14—C15	122.7 (4)	N1—C6—C7	116.7 (4)
N13—C14—C18	115.7 (4)	N1—C6—C5	121.5 (4)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1$A\cdots$Br1	0.80	2.68	3.471 (6)	170
O1W—H1$B\cdots$N1$^{\rm i}$	0.80	2.06	2.848 (6)	169
N2—H2$A\cdots$N3$^{\rm ii}$	0.86	2.19	3.045 (6)	175
N2—H2$B\cdots$O1$W^{\rm iii}$	0.86	2.18	2.926 (6)	145
N11—H11$\cdots$Br1$^{\rm iv}$	0.86	2.41	3.248 (5)	164
N12—H12$A\cdots$N13$^{\rm v}$	0.86	2.13	2.993 (6)	177
N12—H12$B\cdots$Br1$^{\rm iv}$	0.86	2.79	3.537 (5)	147

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

All H atoms (except those of the water molecule) were positioned geometrically and were treated as riding atoms, with C—H and N—H distances of 0.96 and 0.86 Å, respectively [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C or N)]. The H atoms of the water molecule were located in a difference Fourier map and included in fixed positions; their isotropic displacement parameters were refined. All methyl groups were allowed to rotate freely about the C—C bonds.

Data collection: *MolEN* (Fair, 1990); cell refinement: *MolEN*; data reduction: *MolEN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *PLATON*97 (Spek, 1997).

PP thanks the University Grant Commission (UGC), New Delhi, India, for financial assistance through the Minor Research Project. SF thanks the Council of Scientific and Industrial Research (CSIR) for the award of a Senior Research Fellowship (SRF) [reference No. 9/475(109)/2002-EMR-I].

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