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Three 2-aminopurine derivatives

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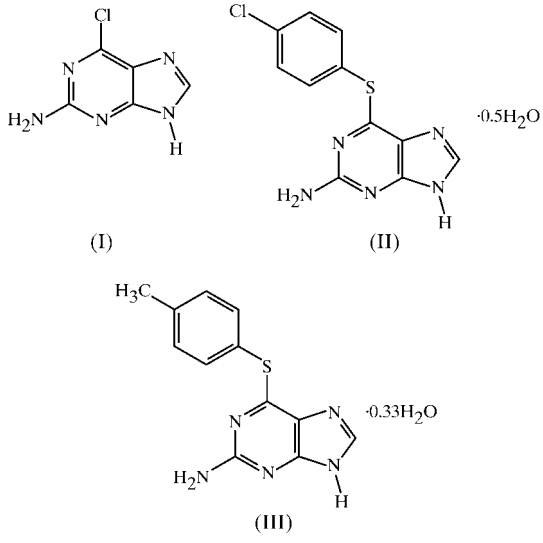
The structure of 2-amino-6-chloropurine, $C_5H_4ClN_5$, (I), comprises a flat molecule, with all possible strong hydrogen-bond donors and acceptors involved in the hydrogen-bonding network. The structures of 2-amino-6-(4-chlorophenylsulfanyl)purine hemihydrate, $C_{11}H_8ClN_5S\cdot0.5H_2O$, (II), and 2-amino-6-(4-methylphenylsulfanyl)purine 0.33-hydrate, $C_{12}H_{11}N_5S\cdot0.33H_2O$, (III), have two and three unique molecules, respectively, and one water molecule in their asymmetric units. Both (II) and (III) exhibit elaborate hydrogen-bonding networks that involve the S (for both) and Cl [for (II)] atoms in addition to the expected strong hydrogen-bonding sites. Both structures also have offset-stacking formations of the phenyl and purine rings.

Comment

Purine bases play an important role in the chemistry of life. Two purine bases, adenine and guanine, are found as major components of DNA and RNA. In these systems, attachment to the deoxyribose or ribose groups occurs *via* N9. Similarly, of the 549 reported structures (Cambridge Structural Database, April 2002 release; Allen, 2002) containing a purine group, the vast majority also contain N9 substituents other than an H atom, with only 92 purine structures exhibiting an N9—H group. There are 34 2-aminopurine structures, of which only two have N9—H groups; these are *N*-(2-amino-6-purinyl)-pyridinium chloride dihydrate (Jaskólski *et al.*, 1987) and



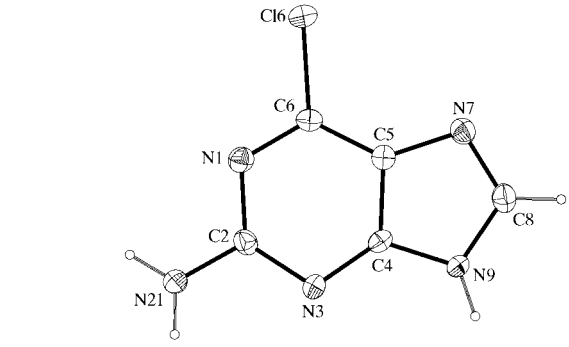


Figure 1
A view of (I) showing the atom-numbering scheme and ellipsoids at the 50% probability level.

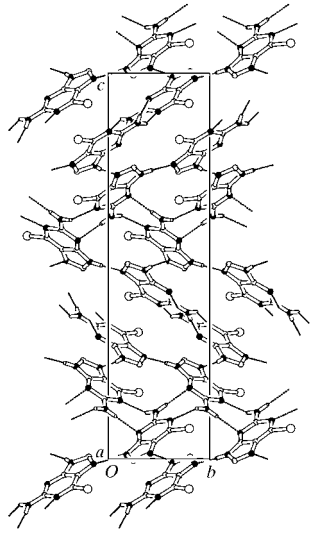


Figure 2
Packing diagram for (I), viewed down the *a* axis, showing both single and pairwise hydrogen-bonding associations (dotted lines) to and from each molecule.

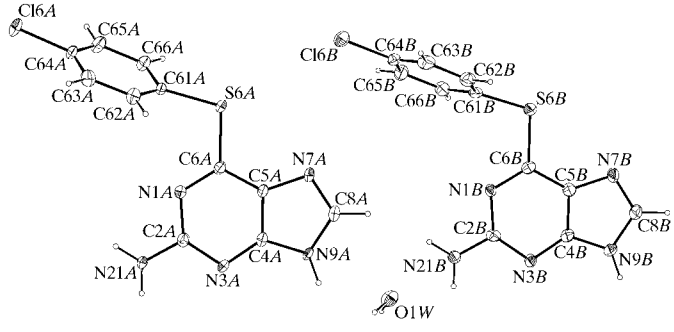


Figure 3
The molecular configuration and atom-numbering scheme for (II), showing ellipsoids at the 50% probability level.

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potassium 2-amino-6-sulfinatopurine monohydrate (Horn & Tiekink, 1995). The hydrogen-bonding patterns in both these 2-aminopurines are dominated by the counter-ions. We report here the crystal structures of three 2-aminopurine derivatives containing N9—H, namely 2-amino-6-chloropurine, (I), 2-amino-6-(4-chlorophenylsulfanyl)purine hemihydrate, (II), and 2-amino-6-(4-methylphenylsulfanyl)purine 0.33-hydrate, (III). Compounds (II) and (III) were both obtained by the nucleophilic addition of a thiophenol derivative to (I).

Compound (I) is a flat molecule [r.m.s. deviation 0.010 (2) Å] with three strong hydrogen-bond donor atoms and three strong hydrogen-bond acceptor atoms (neglecting the N atom in the NH_2 group); the Cl atom can be considered as a weak acceptor (Fig. 1). This equality in numbers of strong hydrogen-bonding agents is reflected in the hydrogen-bonding network with all possible strong hydrogen-bonding sites occupied (Table 1). The N9—H group associates with atom N7 and creates a flat hydrogen-bond chain with molecules of alternating directions inclined to the (001) plane (Fig. 2). Associations between atoms N2, N31 and N4 form a convoluted hydrogen-bonded ribbon network similar to 2-aminopyrimidine and subsequent derivatives (Lynch *et al.*, 2002). Thus, each molecule associates with two molecules *via* pairwise interactions and with two others through single interactions. The Cl atom resides in a position that is approached by H8($1 + y, x, -z$) [Cl···H8 = 3.121 (3) Å], but the distance is too far to be considered a formal C—H···Cl close contact.

The asymmetric unit of (II) consists of two unique 2-amino-6-(4-chlorophenylsulfanyl)purine molecules and one water molecule (Fig. 3). This combination gives eight strong hydrogen-bond donors and seven strong acceptors per asymmetric unit (neglecting the N atoms of the NH_2 groups), plus two S atoms and two Cl atoms, both considered to act as weak hydrogen-bond acceptors. All of these sites are involved in the hydrogen-bonding array, except for two acceptors, N1*B* and

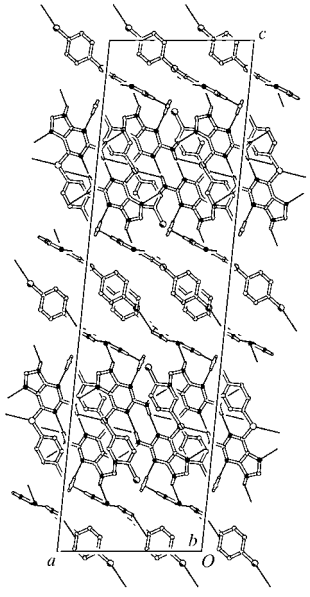

Figure 4
Packing diagram for (II), viewed down the *b* axis, showing the stacking arrangements and a portion of the complex hydrogen-bonding network.

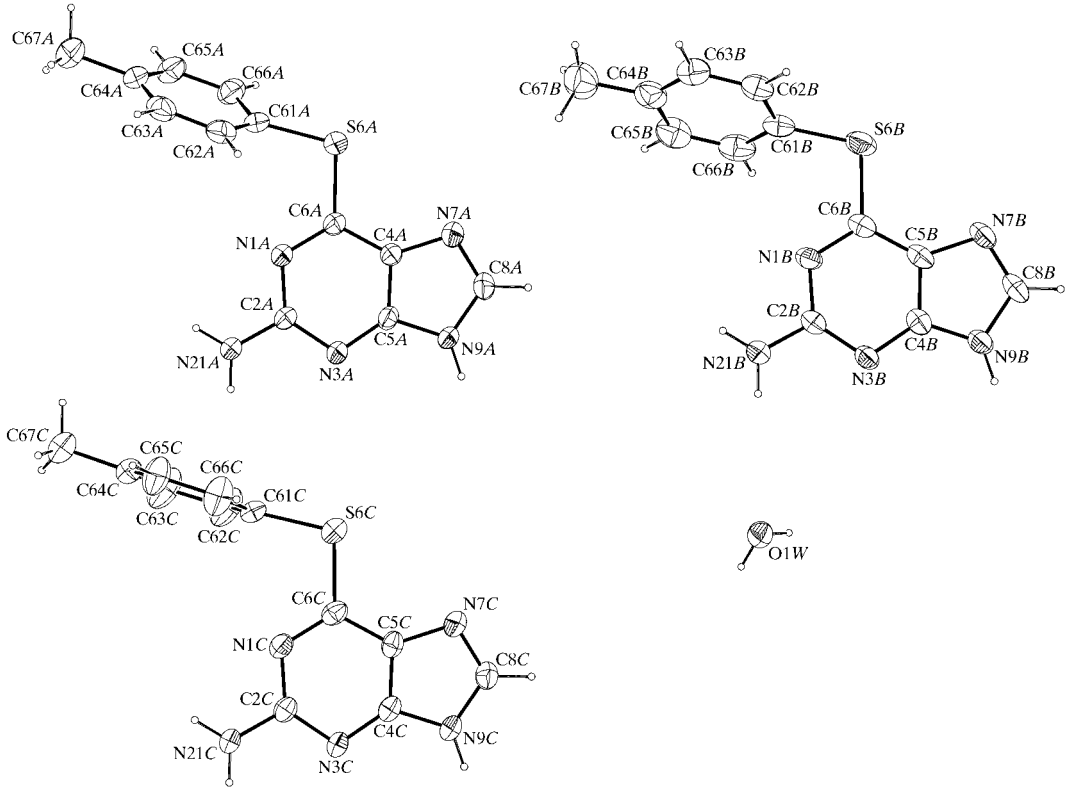

Figure 5
The molecular configuration and atom-numbering scheme for (III), showing ellipsoids at the 50% probability level.

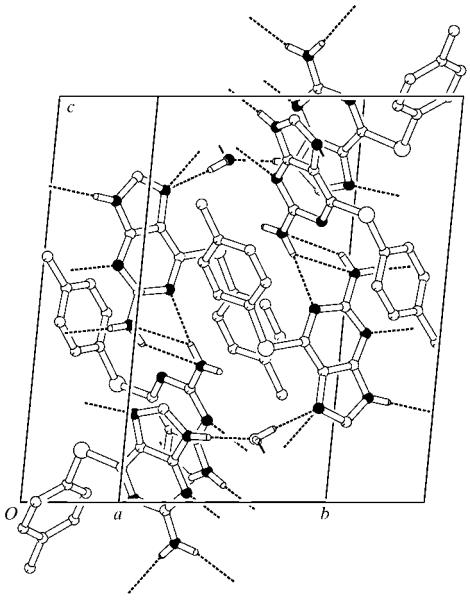

Figure 6
Packing diagram of (III), showing the stacking arrangements and the major hydrogen-bonding associations.

Cl6*A* (Table 2), although the Cl atom is approached by H8*B*($-1+x, 1+y, z$) [Cl···H8*B* = 2.733 (3) Å]. Molecules *A* and *B* and the water molecule form a hydrogen-bonded ring [graph set $R_3^3(10)$; Bernstein *et al.*, 1995] through N9*A*—H···N3*B*, N9*B*—H···O1*W* and O1*W*—H···N3*A* hydrogen bonds. The 2-amino group of molecule *A* associates with atom N7*A* through one H atom and with both N1*A* and S6*A* through the H atom. The 2-amino group of molecule *B* is involved in a similar arrangement, with one H atom associating with N7*B* and the other associating with both Cl6*B* and S6*B*. The remaining water H atom also associates with S6*B*. The resulting network is very complex and difficult to represent in a single-view packing diagram (Fig. 4). The phenyl rings are significantly inclined to the purine rings, with respective dihedral angles for molecules *A* and *B* of 72.21 (6) and 79.57 (8)°. Such angles allow the phenyl rings of molecule *A* to form alternating offset stacks with the purine rings of like molecules [interlayer distances of *ca* 3.40 (4) Å and an interlayer angle of 2.26 (2)°]. For molecule *B*, the offset stacks are only formed by symmetry-related phenyl rings of alternating directions [interlayer distance 3.483 (3) Å], which are coplanar by symmetry.

The asymmetric unit of (III) consists of three unique 2-amino-6-(4-methylphenylsulfanyl)purine molecules and one water molecule (Fig. 5). This combination gives eight strong hydrogen-bond donors, seven strong acceptors (neglecting the N atoms of the NH_2 groups) and three S atoms. Molecules *A* and *B* associate *via* a single hydrogen bond (N9*A*—H···N7*B*) and also *via* an N21*A*—H···N3*A* dimer to form a linked tetramer that is 'capped' at both ends by an association from N9*B*—H to the water molecule. This water molecule, O1*W*, through one H atom, then associates to N7*C*. Molecule *C*, through N9*C*—H and N3*C*, forms a dimer with N3*B* and N21*B*—H. A full list of the hydrogen bonds in (III) is given in Table 3; additional noteworthy interactions are the two three-centre associations, one from N21*C* to N1*A* and N21*A* (note the use in this structure of a NH_2 group as a hydrogen-bond acceptor) and the other from the water molecule to atoms N7*A* and S6*A*. There are no close contacts with one H atom of N21*C*. Again, the hydrogen-bonding network is very extensive and difficult to represent in a single-view packing diagram (Fig. 6). The dihedral angles between the phenyl ring and purine system for molecules *A*, *B* and *C* are 73.08 (7), 63.21 (8) and 80.80 (8)°, respectively, and again allow for offset stacks. A triplet of phenyl-*A*, purine-*C* and purine-*B* has respective interlayer distances and angles of 3.2 (2) Å and 12.34 (4)°, and 3.4 (1) Å and 15.92 (4)°, whereas a tetramer of purine-*A*, phenyl-*C*, phenyl-*C* and purine-*A* has similar values of 3.62 (4) Å and 15.46 (4)°, and 3.679 (3) Å and 0.02 (4)°. The only ring system not to partake in stacking arrangements is phenyl-*B*.

Experimental

All compounds were obtained from Key Organics Ltd and crystals were grown from ethanol solutions.

Compound (I)

Crystal data

$C_5H_4ClN_5$
M_r = 169.58
Tetragonal, $P4_12_12$
a = 7.0855 (10) Å
c = 26.990 (5) Å
V = 1355.0 (4) Å^3
Z = 8
D_x = 1.663 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8615 reflections
θ = 2.9–27.5°
μ = 0.49 mm^{-1}
T = 150 (2) K
Rectangular prism, colourless
0.15 × 0.08 × 0.07 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.910, T_{max} = 0.964
4943 measured reflections
1535 independent reflections
1151 reflections with $I > 2\sigma(I)$
R_{int} = 0.065
θ_{max} = 27.5°
$h = -9 \rightarrow 9$
$k = -5 \rightarrow 9$
$l = -24 \rightarrow 34$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.083
S = 1.04
1535 reflections
100 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0335P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Absolute structure: Flack (1983), 548 Friedel pairs
Flack parameter = 0.00 (10)

Table 1
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N21—H21···N1^{i}	0.88	2.22	3.019 (3)	150
N21—H22···N3^{ii}	0.88	2.15	3.027 (3)	174
N9—H9···N7^{iii}	0.88	2.02	2.888 (3)	168

Symmetry codes: (i) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{4}-z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4}-z$; (iii) $y, x-1, -z$.

Compound (II)

Crystal data

$C_{11}H_8ClN_5S\cdot0.5H_2O$
M_r = 286.74
Monoclinic, $C2/c$
a = 13.353 (3) Å
b = 7.743 (2) Å
c = 47.60 (1) Å
β = 95.85 (3)°
V = 4896 (2) Å^3
Z = 16
D_x = 1.556 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 11 629 reflections
θ = 2.9–27.5°
μ = 0.48 mm^{-1}
T = 120 (2) K
Plate, colourless
0.20 × 0.16 × 0.05 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.737, T_{max} = 0.982
10 871 measured reflections
3842 independent reflections
3045 reflections with $I > 2\sigma(I)$
R_{int} = 0.060
θ_{max} = 25.0°
$h = -15 \rightarrow 15$
$k = -9 \rightarrow 9$
$l = -56 \rightarrow 56$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.105
S = 1.11
3842 reflections
342 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.058P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.57 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N21A—H21A···N7A^{i}	0.88	2.22	3.072 (3)	163
N21A—H22A···N1A^{ii}	0.88	2.49	3.300 (3)	154
N21A—H22A···S6A^{i}	0.88	2.84	3.326 (2)	117
N9A—H9A···N3B^{iii}	0.88	2.19	2.965 (3)	146
N21B—H21B···N7B^{iv}	0.88	2.25	3.077 (3)	158
N21B—H22B···Cl6B^{v}	0.88	2.72	3.475 (2)	145
N21B—H22B···S6B^{iv}	0.88	2.92	3.415 (2)	118
N9B—H9B···O1W^{vi}	0.88	1.89	2.757 (3)	166
O1W—H1W···S6B^{iv}	0.84 (4)	3.05 (4)	3.668 (2)	132 (3)
O1W—H2W···N3A^{vii}	0.85 (4)	1.91 (4)	2.756 (3)	174 (3)

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

Compound (III)

Crystal data

$C_{12}H_{11}N_5S\cdot0.33H_2O$
M_r = 263.32
Triclinic, $P\overline{1}$
a = 10.8074 (2) Å
b = 11.6355 (3) Å
c = 15.3922 (3) Å
α = 85.468 (2)°
β = 83.265 (1)°
γ = 79.7992 (9)°
V = 1888.46 (7) Å^3
Z = 6
D_x = 1.389 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 40 289 reflections
θ = 2.9–27.5°
μ = 0.25 mm^{-1}
T = 150 (2) K
Plate, colourless
0.12 × 0.12 × 0.01 mm

Data collection

Bruker–Nonius KappaCCD area detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.931, T_{max} = 0.998
36 016 measured reflections
8568 independent reflections
4357 reflections with $I > 2\sigma(I)$
R_{int} = 0.111
θ_{max} = 27.5°
$h = -14 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -19 \rightarrow 19$

Table 3
Hydrogen-bonding geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
N21A—H21A···N3A^{i}	0.88	2.17	3.046 (3)	173
N21A—H22A···N21C	0.88	2.46	3.226 (3)	146
N9A—H9A···N7B^{i}	0.88	2.09	2.948 (3)	164
N21B—H21B···N3C^{ii}	0.88	2.20	3.062 (3)	168
N21B—H22B···N7A^{iii}	0.88	2.34	3.204 (3)	168
N9B—H9B···O1W	0.88	1.89	2.765 (3)	173
N21C—H22C···N1A	0.88	2.27	3.130 (3)	164
N21C—H22C···N21A	0.88	2.55	3.226 (3)	134
N9C—H9C···N3B^{ii}	0.88	1.96	2.833 (3)	174
O1W—H1W···N7A^{iv}	0.85 (4)	2.23 (4)	3.075 (3)	171 (3)
O1W—H1W···S6A^{iv}	0.85 (4)	3.05 (3)	3.452 (2)	112 (3)
O1W—H2W···N7C^{v}	0.86 (4)	2.01 (4)	2.863 (3)	174 (3)

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.128
S = 0.94
8568 reflections
507 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

All H atoms were included in the refinement at calculated positions as riding models, with C—H set at 0.95 (Ar–H) and 0.98 Å (CH_3), and N—H set at 0.88 Å, except for the water H atoms, which were located in difference syntheses and for which both positional and displacement parameters were refined. A high R_{int} value of 0.111 for (III) results from the weak high-angle data.

For all compounds, data collection, cell refinement and data reduction: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLUTON*94 (Spek, 1994) and *PLATON*97 (Spek, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1512). Services for accessing these data are described at the back of the journal.

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