

6-(2-Bromobenzylamino)purine monohydrate

Zdeněk Trávníček^{a,b*} and
Christopher J. Rosenker^{c,a}^aDepartment of Inorganic Chemistry, Faculty of Science, Palacký University, Křížkovského 10, CZ-771 47 Olomouc, Czech Republic,^bLaboratory of Growth Regulators, Palacký University, and Institute of Experimental Botany, AS CR, Palacký University, Šlechtitelů 11, CZ-783 71 Olomouc, Czech Republic, and ^cDepartment of Chemistry, Juniata College, 1700 Moore Street, Huntingdon, PA 16652, USACorrespondence e-mail:
zdenek.travnicek@upol.cz

Key indicators

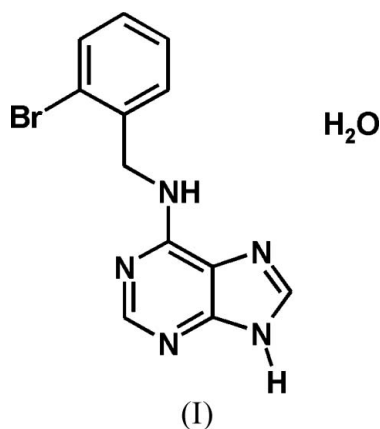
Single-crystal X-ray study
 $T = 110$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
Disorder in solvent or counterion
 R factor = 0.036
 wR factor = 0.106
Data-to-parameter ratio = 12.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The structure of the title compound, $\text{C}_{12}\text{H}_{12}\text{N}_5\text{BrO}\cdot\text{H}_2\text{O}$, consists of discrete molecules connected by $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds to form centrosymmetric dimers, with an $\text{N}\cdots\text{N}$ distance of 2.839 (4) Å. The solvent water molecules are linked by intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds into infinite chains along the [001] direction. The water molecules with disordered H atoms also participate in $\text{O}-\text{H}\cdots\text{O}$, $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds, with $\text{O}\cdots\text{O}$, $\text{N}\cdots\text{O}$ and $\text{O}\cdots\text{N}$ distances of 2.728 (5) and 2.732 (5), 3.107 (3) and 2.748 (3) Å, respectively. In addition to conventional hydrogen bonds, there are several weak interatomic contacts of the type $\text{C}\cdots\text{Br}$, and π -stacking interactions of the types $\text{C}\cdots\text{C}$ and $\text{N}\cdots\text{C}$.

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Comment

The correlation between the structures and biological activities of plant growth hormones (cytokinins) and cyclin-dependent kinase inhibitors (CDKs) derived from 6-benzylaminopurine is under systematic investigation (Trávníček *et al.*, 2001; Trávníček & Kryštof, 2004; Szučová *et al.*, 2006). To expand on previous studies concerning the X-ray structures of known cytokinins and CDKs, the structure of the title compound, (I), has been elucidated.



The structure of (I) (Fig. 1) contains 6-(2-bromobenzylamino)purine (BAP) molecules with nearly planar benzene (A), pyrimidine (B), and imidazole (C) ring systems, with maximum deviations from the mean planes of 0.005 (3) for atom C10, 0.013 (3) for atom C6 and 0.005 (3) Å for atom C5 (DIAMOND; Brandenburg, 2006). Atoms forming the purine system (B+C) also deviate slightly from planarity, the greatest deviation being 0.020 (3) Å for atom N1. Planes B and C are nearly coplanar, with a dihedral angle of 1.3 (1)°. The mean

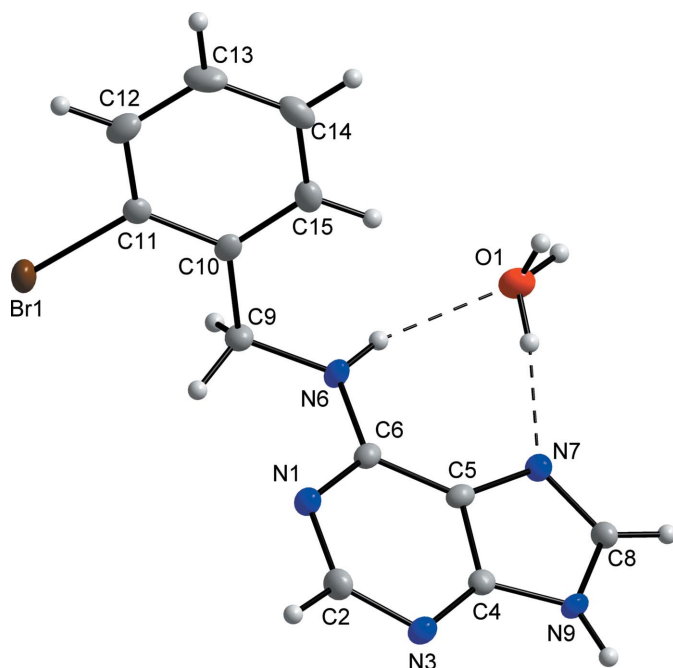


Figure 1
The asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level. Dashed lines indicate hydrogen bonds. One of the water H atoms was treated as disordered over two positions with equal occupancies (both are shown).

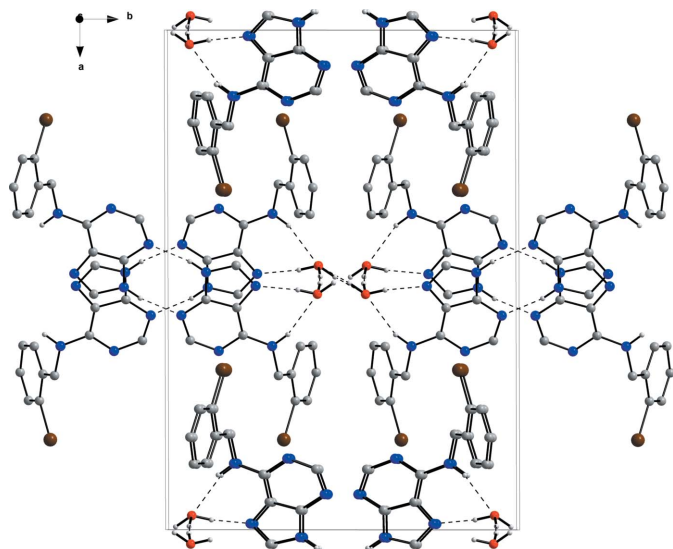


Figure 2
Part of the crystal packing of (I). Dashed lines indicate hydrogen bonds. Some H atoms have been omitted for clarity.

planes of the nearly planar benzene ring (*A*) and purine system (*B*+*C*) make a dihedral angle of $70.23(9)^\circ$. If *CgA*, *CgB* and *CgC* are the centroids of rings *A*, *B* and *C*, respectively, then the *CgA*...*CgB*, *CgA*...*CgC* and *CgB*...*CgC* distances are subsequently $5.7757(4)$, $6.8687(5)$ and $2.0802(1)$ Å. The bond lengths and angles in (I) (Table 1) are quite comparable with those found for 6-(benzylamino)purine (Raghunathan *et al.*, 1983), 6-(2-chlorobenzylamino)purine (Trávníček *et al.*, 2001), and 6-(2-chloro-4-fluorobenzylamino)purine (Trávníček *et al.*, 2006).

The crystal structure of (I) is stabilized by N—H...N hydrogen bonds connecting two adjacent BAP molecules to form centrosymmetric dimers (Fig. 2 and Table 2). The BAP molecule is also connected through O—H...N and N—H...O hydrogen bonds to one solvent water molecule. The water molecules, each with one H atom disordered, are linked by $O_{\text{water}}\text{—H}\cdots O_{\text{water}}$ hydrogen bonds into infinite chains along the [001] direction. Part of the crystal structure of (I) is depicted in Fig. 2.

In addition to conventional hydrogen bonds, there are several weak interatomic contacts of the type C...Br [*C5*...*Br1*^{iv} = $3.517(3)$ and *C6*...*Br1*^{iv} = $3.377(3)$ Å; symmetry code: (iv) $-x + \frac{3}{2}, -y + 1, -z + 2$] and π - π stacking interactions of the type N...C and C...C [*N9*...*C6*^v = $3.713(4)$, *C4*...*C4*^v = $3.320(5)$ and *C8*...*C6*^v = $3.383(4)$ Å; symmetry code: (v) $-x + 1, y, -z + \frac{3}{2}$].

Experimental

All chemicals were acquired from commercial sources: 6-chloropurine (Sigma), Et₂O and *n*-BuOH (Lachema), and Et₃N and 2-bromobenzylamine hydrochloride (Acros Organics). The title compound was prepared from a mixture of 6-chloropurine (23 mmol) and 2-bromobenzylamine hydrochloride (20 mmol) in *n*-butanol (130 ml), to which Et₃N (10 ml, 72 mmol) was added. The reaction mixture was heated to 363 K and stirred for 4.5 h. The mixture was then chilled to 273 K. After 16 h, the resulting precipitate was filtered off and washed with cold H₂O (50 ml) and Et₂O (30 ml). The mother liquor was allowed to evaporate for approximately 5 d, during which time pale-yellow microcrystals containing several well developed single crystals, suitable for X-ray analysis, formed and were separated by filtration. The crystals were washed with Et₂O and dried for 1 h at 343 K.

Crystal data

$C_{12}H_{10}BrN_5 \cdot H_2O$
 $M_r = 322.18$
Monoclinic, *C2/c*
 $a = 21.9381(15)$ Å
 $b = 15.1277(15)$ Å
 $c = 7.6320(5)$ Å
 $\beta = 100.877(9)^\circ$
 $V = 2487.4(3)$ Å³

$Z = 8$
 $D_x = 1.721$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 3.31$ mm⁻¹
 $T = 110(2)$ K
Prism, colourless
 $0.35 \times 0.25 \times 0.25$ mm

Data collection

Oxford Xcalibur diffractometer
 ω scans
Absorption correction: multi-scan (Blessing, 1995)
 $T_{\min} = 0.399$, $T_{\max} = 0.438$

8154 measured reflections
2192 independent reflections
2034 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$
 $\theta_{\max} = 25.1^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.106$
 $S = 1.14$
2192 reflections
181 parameters

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0683P)^2 + 3.1343P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.73$ e Å⁻³
 $\Delta\rho_{\min} = -0.42$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

| | | | |
|--------------|-----------|---------------|-----------|
| Br1—C11 | 1.901 (3) | N7—C8 | 1.311 (4) |
| N1—C2 | 1.333 (4) | N7—C5 | 1.378 (4) |
| N1—C6 | 1.347 (4) | N9—C8 | 1.349 (4) |
| N3—C2 | 1.326 (4) | N9—C4 | 1.366 (4) |
| N3—C4 | 1.346 (4) | C4—C5 | 1.383 (4) |
| N6—C6 | 1.353 (4) | C5—C6 | 1.406 (4) |
| N6—C9 | 1.429 (4) | | |
| | | | |
| C2—N1—C6 | 118.4 (3) | N3—C4—C5 | 126.1 (3) |
| C2—N3—C4 | 111.2 (3) | N9—C4—C5 | 105.8 (3) |
| C6—N6—C9 | 122.9 (3) | N7—C5—C4 | 110.1 (3) |
| C8—N7—C5 | 104.0 (2) | N7—C5—C6 | 133.1 (3) |
| C8—N9—C4 | 106.1 (3) | C4—C5—C6 | 116.9 (3) |
| N3—C2—N1 | 129.2 (3) | N1—C6—C5 | 118.1 (3) |
| N3—C4—N9 | 128.0 (3) | N7—C8—N9 | 113.9 (3) |
| | | | |
| C9—N6—C6—N1 | −6.8 (4) | N6—C9—C10—C15 | 9.4 (4) |
| C6—N6—C9—C10 | 106.9 (3) | | |

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

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| N6—H6A...O1 | 0.88 | 2.25 | 3.107 (4) | 163 |
| O1—H1W...N7 | 0.89 (3) | 1.86 (3) | 2.748 (3) | 172 (5) |
| N9—H9A...N3 ⁱ | 0.88 | 1.97 | 2.838 (4) | 169 |
| O1—H1VA...O1 ⁱⁱ | 0.93 (3) | 1.81 (3) | 2.728 (5) | 170 (8) |
| O1—H1VB...O1 ⁱⁱⁱ | 0.92 (3) | 1.83 (3) | 2.732 (5) | 167 (9) |

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

All H atoms of the organic molecule were located in a difference map and refined using a riding model, with C—H distances of 0.95 and 0.99 Å, N—H distances of 0.88 Å, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. H

atoms attached to atom O1 were refined freely with a fixed U_{eq} parameter. Atom H1V, involved in the O1—H1VA...O1ⁱⁱ and O1—H1VB...O1ⁱⁱⁱ intermolecular hydrogen bonds [symmetry codes: (ii) $-x + 1, y, -z + \frac{3}{2}$, (iii) $-x + 1, -y + 1, -z + 2$], was treated as disordered over two positions with equal occupancies.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2002); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97* and *DIAMOND*.

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