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5-Bromo-1,2,4-triazolo[1,5-*a*]pyrimidine

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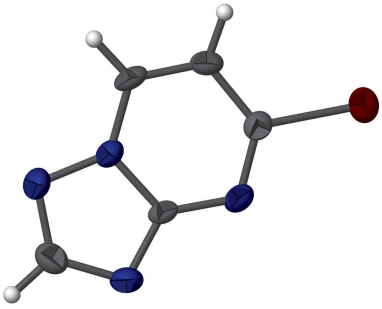
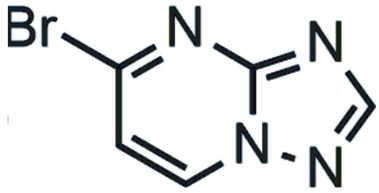
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_5H_3BrN_4$, the almost planar triazolopyrimidine ring system (r.m.s. deviation = 0.014 Å) carries a bromo substituent at the 5-position. In the crystal, C—H···N hydrogen bonds form inversion dimers enclosing $R_2^2(8)$ rings and also link molecules into $C(5)$ chains along the *c*-axis direction. Br···N halogen bonds [3.185 (4) Å], π–π stacking interactions, centroid-to-centroid separation [3.663 (3) Å] and C—Br···π contacts [Br···Cg = 3.7881 (17) Å] are also found and combine with the C—H···N hydrogen bonds to stack the molecules along the *a*-axis direction.

3D view



Chemical scheme



Structure description

In a continuation of our work on the synthesis and structure determination of 1,2,4-triazolo[1,5-*a*]pyrimidine derivatives (Gilandoust *et al.*, 2016), the title compound was prepared and its structure is reported here, Fig. 1. The triazolopyrimidine ring system is planar (as expected) with an r.m.s. deviation of 0.014 Å. Bond lengths and angles in the ring system are normal and similar to those found in the related compound 5-(2-ethoxy-4-fluorophenyl-1,2,4-triazolo[1,5-*a*]pyrimidine (Gilandoust *et al.*, 2016).

In the crystal, C5—H5···N3 contacts, Table 1, form inversion dimers and generate $R_2^2(6)$ rings. C1—H1···N1 hydrogen bonds form $C(5)$ chains of molecules along *c*. These contacts combine with Br1···N4^{iii} halogen bonds [d(Br···N) = 3.185 (4) Å; symmetry code: (iii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$] to form stacked layers of molecules in the *bc* plane, Fig. 2. Stacking along the *a*-axis direction is aided further by a combination of offset π–π stacking interactions [$Cg1\cdots Cg2^{iv}$ = 3.663 (3) Å; symmetry code: (iv) $-1+x, y, z$; $Cg1$ and $Cg2$ are the centroids of the C4/N2/N3/C5/N4 and C1–C3/N1/C4/N2 rings, respectively] reinforced by unusual, but not unprecedented (Shukla *et al.*, 2017), C3—

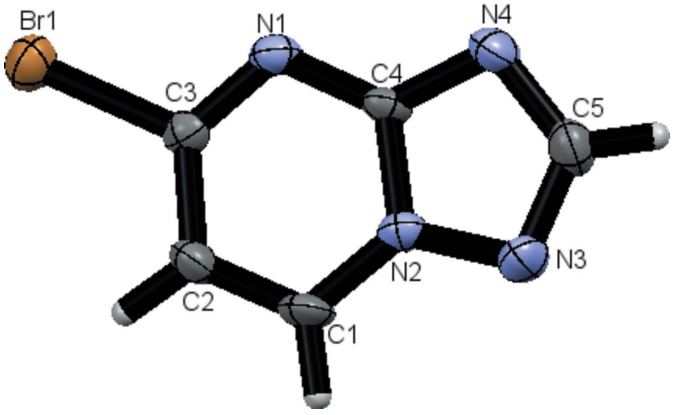


Figure 1
A view of the title molecule, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

Br1···*Cg*2^{v} contacts [Br···*Cg*1 = 3.7881 (17) Å, C3—Br1···*Cg*2 = 67.60 (12)°; symmetry code: (v) $x+1, y, z$;] , Fig. 3. Overall, a three-dimensional network of molecules stacked along the *a*-axis direction forms as a result of these contacts, Fig. 4.

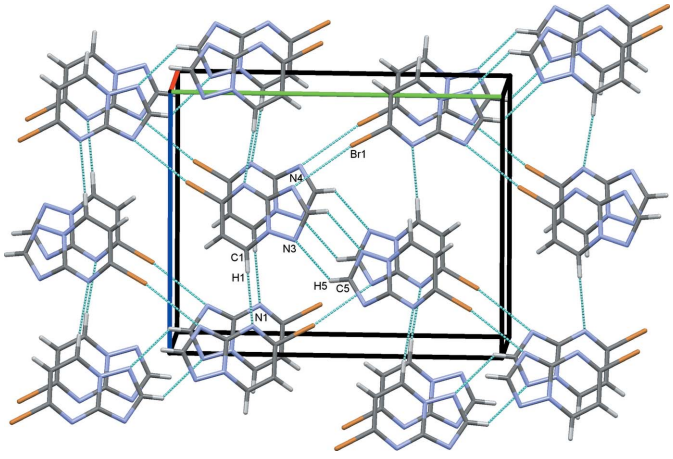


Figure 2
Layers of molecules in the *bc* plane. Hydrogen and halogen bonds are drawn as blue dashed lines.

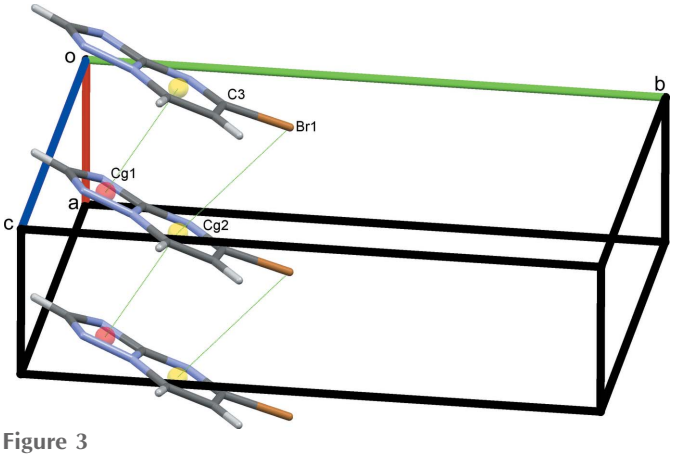


Figure 3
Offset π–π contacts and C—Br···π interactions (green dotted lines), with ring centroids shown as coloured spheres.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···N1^{i}	0.93	2.52	3.421 (6)	164
C5—H5···N3^{ii}	0.93	2.61	3.321 (6)	133

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_5H_3BrN_4$
M_r	199.02
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	293
a, *b*, *c* (Å)	3.9511 (4), 14.3306 (11), 11.367 (1)
β (°)	94.574 (8)
V (Å^3)	641.57 (9)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	6.32
Crystal size (mm)	0.31 × 0.24 × 0.23
Data collection	
Diffractometer	Rigaku Saturn724+
Absorption correction	Multi-scan (*NUMABS*; Rigaku, 1999)
T_{min}, T_{max}	0.244, 0.323
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2438, 1129, 977
R_{int}	0.036
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.111, 1.08
No. of reflections	1129
No. of parameters	92
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.78, −0.48

Computer programs: *CrystalClear SM Expert* (Rigaku, 2011), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008) and *OLEX2* (Dolomanov *et al.*, 2009).

Synthesis and crystallization

5-Bromo-2-hydrazinopyrimidine (0.95 mmol) and formaldehyde (1.00 mmol) were suspended in EtOH (5 ml), and stirred for 2 h at RT. The reaction mixture was concentrated under

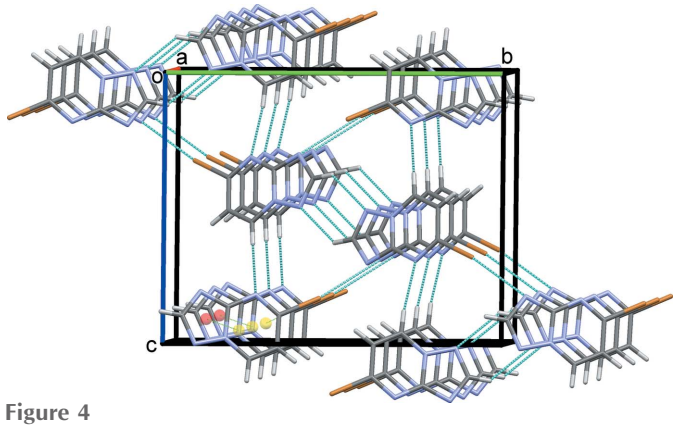


Figure 4
The overall packing, viewed along the *a* axis, showing π–π contacts and C—Br···π interactions.

reduced pressure to remove the ethanol and the crude product purified by column chromatography using 60:120 mesh silica gel and a MeOH: dichloromethane solution (10:90 ml) as eluent to yield 5-bromo-2-(2-methylenehydrazinyl) pyrimidine as a beige solid. 5-Bromo-2-(2-methylenehydrazinyl)-pyrimidine (0.78 mmol) dissolved in (5 ml) dichloromethane and iodobenzene diacetate (0.78 mmol) was added in one portion. The mixture was stirred for 15 h at RT and the solvent evaporated. The residue was titurated with Et_2O (5 ml), filtered and chromatographed using 60:120 mesh silica gel and MeOH:dichloromethane (10:90 ml) as eluent to give 5-bromo-[1,2,4]triazolo[1,5-*a*]pyrimidine as a yellow solid. Good quality single crystals suitable for X-ray diffraction studies were obtained by the slow evaporation method using ethanol as solvent.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x161944 [https://doi.org/10.1107/S2414314616019441]

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Crystal data

$C_5H_3BrN_4$
M_r = 199.02
Monoclinic, $P2_1/n$
a = 3.9511 (4) Å
b = 14.3306 (11) Å
c = 11.367 (1) Å
β = 94.574 (8)°
V = 641.57 (9) Å^3
Z = 4
$F(000)$ = 384
D_x = 2.060 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1129 reflections
θ = 2.3–25.0°
μ = 6.32 mm^{-1}
T = 293 K
Colourless, block
0.31 × 0.24 × 0.23 mm

Data collection

Rigaku Saturn724+ diffractometer
profile data from ω–scans
Absorption correction: multi-scan (NUMABS; Rigaku, 1999)
T_{min} = 0.244, T_{max} = 0.323
2438 measured reflections
1129 independent reflections
977 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 25.0°, θ_{min} = 2.3°
h = −4→3
k = −16→17
l = −13→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.111
S = 1.08
1129 reflections
92 parameters
0 restraints
Primary atom site location: iterative
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0649P)^2 + 0.2378P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.78 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.017 (4)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.37251 (12)	0.44459 (3)	0.83589 (4)	0.0390 (3)
N2	−0.1257 (9)	0.1890 (2)	0.9772 (3)	0.0275 (8)
N1	0.1085 (9)	0.2690 (2)	0.8197 (3)	0.0291 (8)
N3	−0.2878 (11)	0.1067 (3)	0.9961 (3)	0.0381 (10)
N4	−0.1505 (10)	0.1167 (3)	0.8052 (3)	0.0360 (10)
C2	0.1125 (11)	0.3336 (3)	1.0154 (4)	0.0322 (10)
H2	0.1769	0.3830	1.0655	0.039*
C3	0.1746 (10)	0.3359 (3)	0.8956 (3)	0.0255 (9)
C1	−0.0434 (12)	0.2578 (3)	1.0557 (4)	0.0347 (11)
H1	−0.0924	0.2530	1.1341	0.042*
C4	−0.0482 (11)	0.1944 (3)	0.8616 (3)	0.0241 (9)
C5	−0.2909 (13)	0.0680 (3)	0.8910 (4)	0.0365 (11)
H5	−0.3859	0.0093	0.8763	0.044*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0447 (4)	0.0354 (4)	0.0366 (4)	−0.00695 (19)	0.0006 (2)	0.00610 (18)
N2	0.0334 (19)	0.0306 (19)	0.0184 (17)	−0.0009 (16)	0.0018 (15)	0.0026 (15)
N1	0.037 (2)	0.031 (2)	0.0200 (18)	0.0021 (16)	0.0045 (16)	0.0020 (15)
N3	0.058 (3)	0.031 (2)	0.025 (2)	−0.0082 (19)	0.0050 (18)	0.0059 (16)
N4	0.053 (3)	0.030 (2)	0.0250 (19)	−0.0032 (18)	0.0038 (18)	−0.0064 (16)
C2	0.042 (3)	0.030 (2)	0.023 (2)	−0.002 (2)	−0.0011 (19)	−0.0063 (18)
C3	0.022 (2)	0.032 (2)	0.023 (2)	0.0001 (17)	−0.0014 (16)	0.0024 (17)
C1	0.052 (3)	0.039 (3)	0.014 (2)	−0.001 (2)	0.004 (2)	−0.0020 (18)
C4	0.031 (2)	0.026 (2)	0.0147 (18)	0.0048 (18)	−0.0008 (16)	−0.0004 (16)
C5	0.042 (3)	0.030 (2)	0.036 (3)	−0.006 (2)	−0.005 (2)	−0.001 (2)

Geometric parameters (Å, º)

Br1—C3	1.893 (4)	N4—C4	1.331 (6)
N2—N3	1.367 (5)	N4—C5	1.354 (6)
N2—C1	1.353 (5)	C2—H2	0.9300
N2—C4	1.375 (5)	C2—C3	1.403 (6)
N1—C3	1.303 (5)	C2—C1	1.347 (6)
N1—C4	1.342 (5)	C1—H1	0.9300
N3—C5	1.316 (6)	C5—H5	0.9300
N3—N2—C4	110.0 (3)	C2—C3—Br1	118.5 (3)
C1—N2—N3	128.0 (3)	N2—C1—H1	121.4
C1—N2—C4	121.9 (4)	C2—C1—N2	117.2 (4)
C3—N1—C4	115.2 (3)	C2—C1—H1	121.4
C5—N3—N2	101.0 (3)	N1—C4—N2	121.9 (4)
C4—N4—C5	102.2 (4)	N4—C4—N2	109.3 (4)
C3—C2—H2	121.0	N4—C4—N1	128.8 (4)

C1—C2—H2	121.0	N3—C5—N4	117.5 (4)
C1—C2—C3	117.9 (4)	N3—C5—H5	121.3
N1—C3—Br1	115.8 (3)	N4—C5—H5	121.3
N1—C3—C2	125.8 (4)		
N2—N3—C5—N4	−0.6 (6)	C1—C2—C3—Br1	176.9 (4)
N3—N2—C1—C2	−178.9 (4)	C1—C2—C3—N1	−3.3 (7)
N3—N2—C4—N1	179.2 (4)	C4—N2—N3—C5	1.0 (5)
N3—N2—C4—N4	−1.2 (5)	C4—N2—C1—C2	1.4 (6)
C3—N1—C4—N2	−1.3 (6)	C4—N1—C3—Br1	−176.6 (3)
C3—N1—C4—N4	179.1 (4)	C4—N1—C3—C2	3.5 (6)
C3—C2—C1—N2	0.6 (6)	C4—N4—C5—N3	−0.1 (6)
C1—N2—N3—C5	−178.7 (4)	C5—N4—C4—N2	0.7 (5)
C1—N2—C4—N1	−1.1 (6)	C5—N4—C4—N1	−179.6 (4)
C1—N2—C4—N4	178.6 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···N1^{i}	0.93	2.52	3.421 (6)	164
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