

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

## 2-Amino-4-(4-bromophenyl)-8-trifluoromethyl-3,4-dihydropyrimido[1,2-a]-[1,3,5]triazin-6(5H)-one<sup>1</sup>

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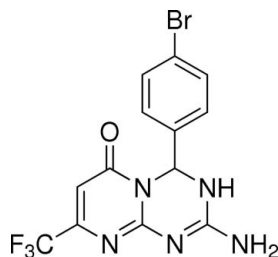
Received 6 February 2009; accepted 2 March 2009

Key indicators: single-crystal X-ray study;  $T = 223$  K; mean  $\sigma(\text{C}-\text{C}) = 0.007$  Å; disorder in main residue;  $R$  factor = 0.052;  $wR$  factor = 0.138; data-to-parameter ratio = 14.6.

The title compound,  $\text{C}_{13}\text{H}_9\text{BrF}_3\text{N}_5\text{O}$ , crystallizes with two independent molecules in the asymmetric unit. The pyrimidine rings of the molecules are planar [maximum deviations 0.053 (3) and 0.012 (3) Å], while the triazine rings adopt flattened half-boat conformations with the *p*-bromophenyl rings in the flagpole positions. The crystal packing is stabilized by a three-dimensional network of intermolecular  $\text{N}-\text{H}\cdots\text{N}$ ,  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{N}-\text{H}\cdots\text{F}$  hydrogen bonds.

### Related literature

For the crystal structure of 7,7-dimethyl-2-phenyl-6,7-dihydro-1,2,4-triazolo[1,5-*a*][1,3,5]triazin-5-amine, see: Dolzhenko *et al.* (2007). For the preparation of benzo-fused analogues, see: Dolzhenko *et al.* (2008*a*). For the previous report in this series, see: Dolzhenko *et al.* (2008*b*).



### Experimental

#### Crystal data

 $\text{C}_{13}\text{H}_9\text{BrF}_3\text{N}_5\text{O}$  $M_r = 388.16$ 

Orthorhombic,  $Pna2_1$   
 $a = 10.0531$  (4) Å  
 $b = 29.9108$  (13) Å  
 $c = 10.1945$  (4) Å  
 $V = 3065.4$  (2) Å<sup>3</sup>

$Z = 8$   
 Mo  $K\alpha$  radiation  
 $\mu = 2.73$  mm<sup>-1</sup>  
 $T = 223$  K  
 $0.46 \times 0.34 \times 0.20$  mm

#### Data collection

Bruker SMART APEX CCD diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2001)  
 $T_{\min} = 0.367$ ,  $T_{\max} = 0.612$   
 (expected range = 0.348–0.580)

20728 measured reflections  
 6287 independent reflections  
 4979 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.037$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$   
 $wR(F^2) = 0.138$   
 $S = 1.04$   
 6287 reflections  
 432 parameters  
 16 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 1.50$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.74$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983), 2044 Friedel pairs  
 Flack parameter: 0.011 (10)

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1N}\cdots\text{N2}^{\text{i}}$	0.87 (2)	2.15 (2)	3.005 (5)	171 (5)
$\text{N5}-\text{H5A}\cdots\text{O2}^{\text{ii}}$	0.895 (14)	2.09 (3)	2.905 (5)	152 (5)
$\text{N5}-\text{H5B}\cdots\text{N4}^{\text{i}}$	0.892 (14)	2.25 (2)	3.095 (6)	159 (5)
$\text{N5}-\text{H5B}\cdots\text{F1}^{\text{i}}$	0.892 (14)	2.46 (4)	3.054 (5)	124 (4)
$\text{N6}-\text{H6N}\cdots\text{N7}^{\text{iii}}$	0.902 (19)	2.10 (3)	2.967 (5)	160 (5)
$\text{N10}-\text{H10A}\cdots\text{O1}$	0.89 (2)	2.03 (3)	2.885 (5)	162 (5)
$\text{N10}-\text{H10B}\cdots\text{N9}^{\text{iii}}$	0.90 (2)	2.15 (2)	3.041 (5)	171 (5)

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

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

This work was supported by the National Medical Research Council, Singapore (grant Nos. NMRC/NIG/0019/2008 and NMRC/NIG/0020/2008).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2543).

### References

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 Dolzhenko, A. V., Tan, G. K., Koh, L. L., Dolzhenko, A. V. & Chui, W. K. (2007). *Acta Cryst.* **E63**, o2796.  
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<sup>1</sup> Part 13 in the series 'Fused heterocyclic systems with an *s*-triazine ring'. For Part 12, see Dolzhenko *et al.* (2008*b*).

**supplementary materials**

*Acta Cryst.* (2009). E65, o684 [ doi:10.1107/S1600536809007612 ]

## 2-Amino-4-(4-bromophenyl)-8-trifluoromethyl-3,4-dihydropyrimido[1,2-*a*][1,3,5]triazin-6(5*H*)-one

A. V. Dolzhenko, N. Sachdeva, G. K. Tan, L. L. Koh and W. K. Chui

### Comment

The title compound was synthesized *via* thermal cyclocondensation of 6-oxo-4-trifluoromethyl-1,6-dihydropyrimidin-2-yl guanidine with *p*-bromobenzaldehyde (Fig. 1) using the methodology that we successfully applied previously for the preparation of its benzofused analogues (Dolzhenko *et al.*, 2008*a*). In general, the synthesized compound might be involved in tautomerism with four possible tautomers (Fig. 2). However, only one tautomeric form *viz.* 2-amino-4-(4-bromophenyl)-8-trifluoromethyl-3,4-dihydro-6*H*-pyrimido[1,2-*a*][1,3,5]triazin-6-one was found in the crystal.

The compound crystallized with two independent molecules (**A** and **B**) in the asymmetric unit (Fig. 3). The pyrimidine rings in the molecules are planar with maximum deviations 0.0525 (26) Å (C3) and 0.0118 (32) Å (C18) from the planes C3/N3/C4—C6/N4 and C16/N8/C17—C19/N9 of molecules **A** and **B**, respectively. Similarly to structurally related 7,7-dimethyl-2-phenyl-6,7-dihydro-1,2,4-triazolo[1,5-*a*][1,3,5]triazin-5-amine (Dolzhenko *et al.*, 2007), the triazine rings in the molecules adopt flattened half-boat conformations with atoms N2 and N7 at the sterns and *sp*<sup>3</sup>-hybridized atoms C1 and C14 at the bows with *p*-bromophenyl rings as flagpoles. However, the molecules are significantly different in the geometry at bridgehead nitrogen atoms (N3 and N8) and *sp*<sup>3</sup>-hybridized atoms C1 and C14 of the triazine rings. The torsion angles C4—N3—C1—N1 and C17—N8—C14—N6 are 136.7 (4)° and 150.4 (3)°, respectively. In molecule **B**, the bond N8—C14 is located almost in the phenyl ring (C21—C26) plane: the torsion angle N8—C14—C21—C26 is 2.6 (5)°. The corresponding torsion angle N3—C1—C8—C9 of molecule **A** is 42.5 (6)°. The N1—C2, N2—C2, N5—C2 bond distances in **A** and N6—C15, N7—C15, N10—C15 in **B** are similar that suggests guanidine-like electron delocalization in N1/N2/N5/C2 and N6/N7/N10/C15 fragments of the molecules.

The crystal packing is stabilized by three-dimensional network of intramolecular N—H⋯N, N—H⋯O and N—H⋯F hydrogen bonds (Table 1, Fig. 4).

### Experimental

2-Amino-4-(4-bromophenyl)-8-trifluoromethyl-3,4-dihydro-6*H*-pyrimido[1,2-*a*][1,3,5]triazin-6-one was synthesized from 6-oxo-4-trifluoromethyl-1,6-dihydropyrimidin-2-yl guanidine and *p*-bromobenzaldehyde according to general method reported by Dolzhenko *et al.* (2008*a*). Single crystals suitable for crystallographic analysis were grown by slow evaporation of the solution in ethyl acetate / methanol.

### Refinement

N-bound H atoms were located in a difference map and refined freely. C-bound H atoms were positioned geometrically (C—H = 0.94 or 0.99 Å) and were constrained in a riding motion approximation with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . One of the BrC<sub>6</sub>H<sub>4</sub> parts is disordered into two parts at 89:11 ratio.

## Figures

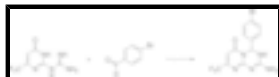


Fig. 1. The synthesis of 2-amino-4-(4-bromophenyl)-8-trifluoromethyl-3,4-dihydro-6H-pyrimido[1,2-*a*][1,3,5]triazin-6-one

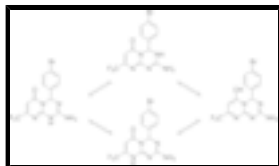


Fig. 2. Tautomerism in the title compound

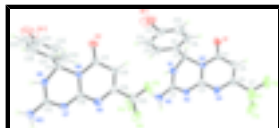


Fig. 3. The molecular structure of 2-amino-4-(4-bromophenyl)-8-trifluoromethyl-3,4-dihydro-6H-pyrimido[1,2-*a*][1,3,5]triazin-6-one with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

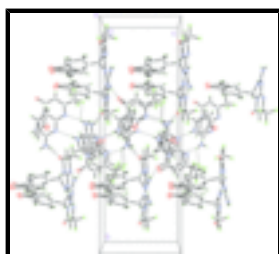


Fig. 4. Molecular parking in the crystal, viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

## 2-Amino-4-(4-bromophenyl)-8-trifluoromethyl-3,4- dihydropyrimido[1,2-*a*][1,3,5]triazin-6(5*H*)-one

### Crystal data

$C_{13}H_9BrF_3N_5O$

$M_r = 388.16$

Orthorhombic,  $Pna2_1$

Hall symbol: P 2c -2n

$a = 10.0531$  (4) Å

$b = 29.9108$  (13) Å

$c = 10.1945$  (4) Å

$V = 3065.4$  (2) Å<sup>3</sup>

$Z = 8$

$F_{000} = 1536$

$D_x = 1.682$  Mg m<sup>-3</sup>

Melting point: 516 K

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 5069 reflections

$\theta = 2.4$ – $25.1^\circ$

$\mu = 2.73$  mm<sup>-1</sup>

$T = 223$  K

Block, colourless

$0.46 \times 0.34 \times 0.20$  mm

### Data collection

Bruker SMART APEX CCD  
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 223$  K

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

6287 independent reflections

4979 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.037$

$\theta_{max} = 27.5^\circ$

$\theta_{min} = 1.4^\circ$

$h = -12 \rightarrow 13$

(SADABS; Sheldrick, 2001)

$T_{\min} = 0.367$ ,  $T_{\max} = 0.612$

20728 measured reflections

$k = -38 \rightarrow 38$

$l = -13 \rightarrow 11$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.052$

$wR(F^2) = 0.138$

$S = 1.04$

6287 reflections

432 parameters

16 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0646P)^2 + 2.1384P]$$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.50 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -0.73 \text{ e } \text{Å}^{-3}$

Extinction correction: none

Absolute structure: Flack (1983), 2044 Friedel pairs

Flack parameter: 0.011 (10)

### Special details

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

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{Å}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	1.0316 (3)	0.34878 (10)	1.2353 (3)	0.0346 (7)	
F1	0.9317 (4)	0.36022 (11)	1.7842 (4)	0.0634 (10)	
F2	0.8409 (4)	0.30866 (11)	1.6709 (4)	0.0750 (12)	
F3	0.7371 (4)	0.37004 (16)	1.7065 (5)	0.0873 (14)	
N1	1.0194 (3)	0.47967 (11)	1.2317 (4)	0.0259 (7)	
H1N	1.012 (5)	0.4927 (15)	1.156 (3)	0.031*	
N2	0.9826 (3)	0.48272 (10)	1.4583 (3)	0.0237 (7)	
N3	1.0181 (3)	0.41352 (10)	1.3521 (3)	0.0232 (7)	
N4	0.9342 (4)	0.41721 (11)	1.5665 (4)	0.0290 (7)	
N5	0.9597 (4)	0.54572 (11)	1.3299 (4)	0.0335 (8)	
H5A	0.919 (5)	0.5568 (15)	1.401 (3)	0.040*	
H5B	0.982 (5)	0.5632 (14)	1.262 (4)	0.040*	

## supplementary materials

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C1	1.0910 (4)	0.43826 (13)	1.2510 (4)	0.0250 (8)	
H1A	1.0904	0.4209	1.1683	0.030*	
C2	0.9892 (4)	0.50251 (13)	1.3412 (4)	0.0249 (8)	
C3	0.9789 (4)	0.43766 (13)	1.4607 (4)	0.0258 (8)	
C4	0.9958 (4)	0.36750 (13)	1.3367 (5)	0.0288 (9)	
C5	0.9359 (5)	0.34747 (15)	1.4486 (5)	0.0387 (10)	
H5	0.9122	0.3171	1.4478	0.046*	
C6	0.9137 (5)	0.37273 (15)	1.5558 (5)	0.0358 (10)	
C7	0.8558 (7)	0.35237 (18)	1.6796 (6)	0.0542 (15)	
C8	1.2338 (4)	0.44558 (14)	1.2947 (5)	0.0279 (9)	
C9	1.3053 (5)	0.41197 (16)	1.3543 (6)	0.0454 (13)	
H9	1.2654	0.3838	1.3664	0.054*	
C10	1.4348 (5)	0.41866 (18)	1.3968 (6)	0.0519 (14)	
H10	1.4826	0.3954	1.4372	0.062*	
C11	1.4917 (4)	0.45984 (18)	1.3788 (6)	0.0441 (12)	
C12	1.4249 (5)	0.49351 (18)	1.3178 (6)	0.0450 (12)	
H12	1.4660	0.5214	1.3044	0.054*	
C13	1.2959 (5)	0.48627 (15)	1.2758 (5)	0.0362 (10)	
H13	1.2495	0.5095	1.2336	0.043*	
Br1	1.66612 (4)	0.47071 (3)	1.44122 (8)	0.0697 (2)	
O2	0.7222 (3)	0.09824 (9)	0.9889 (3)	0.0338 (7)	
F4	1.2813 (4)	0.10516 (13)	1.0040 (5)	0.0782 (13)	
F5	1.1837 (3)	0.05015 (8)	1.0941 (4)	0.0578 (10)	
F6	1.2446 (3)	0.10589 (11)	1.2081 (5)	0.0631 (10)	
N6	0.7243 (3)	0.22885 (11)	1.0553 (4)	0.0271 (8)	
H6N	0.653 (3)	0.2463 (13)	1.073 (5)	0.032*	
N7	0.9576 (3)	0.22901 (10)	1.0690 (4)	0.0261 (7)	
N8	0.8395 (3)	0.16152 (10)	1.0287 (4)	0.0237 (7)	
N9	1.0675 (3)	0.16188 (11)	1.0790 (4)	0.0288 (8)	
N10	0.8364 (4)	0.29270 (11)	1.1091 (4)	0.0319 (8)	
H10A	0.909 (3)	0.3050 (15)	1.144 (5)	0.038*	
H10B	0.762 (3)	0.3090 (15)	1.104 (6)	0.038*	
C20	1.1928 (5)	0.09342 (14)	1.0926 (6)	0.0377 (11)	
C14	0.7273 (4)	0.18807 (12)	0.9806 (5)	0.0258 (9)	
H14	0.6443	0.1713	0.9985	0.031*	
C15	0.8407 (4)	0.25037 (12)	1.0759 (4)	0.0231 (8)	
C16	0.9555 (4)	0.18357 (12)	1.0582 (4)	0.0246 (8)	
C17	0.8279 (4)	0.11509 (13)	1.0201 (4)	0.0255 (8)	
C18	0.9505 (4)	0.09218 (13)	1.0451 (5)	0.0287 (9)	
H18	0.9540	0.0608	1.0441	0.034*	
C19	1.0602 (4)	0.11631 (13)	1.0699 (4)	0.0291 (9)	
Br2	0.74894 (14)	0.22662 (3)	0.38715 (10)	0.0924 (5)	0.899 (3)
C21	0.7359 (4)	0.19636 (19)	0.8349 (3)	0.0312 (13)	0.899 (3)
C22	0.6379 (4)	0.22284 (19)	0.7782 (4)	0.0475 (14)	0.899 (3)
H22	0.5695	0.2348	0.8304	0.057*	0.899 (3)
C23	0.6409 (4)	0.23160 (16)	0.6443 (4)	0.0599 (19)	0.899 (3)
H23	0.5747	0.2495	0.6060	0.072*	0.899 (3)
C24	0.7420 (4)	0.21389 (14)	0.5671 (3)	0.0509 (16)	0.899 (3)
C25	0.8400 (4)	0.18741 (14)	0.6238 (3)	0.0621 (19)	0.899 (3)

H25	0.9084	0.1754	0.5716	0.075*	0.899 (3)
C26	0.8370 (4)	0.17865 (16)	0.7577 (3)	0.0463 (16)	0.899 (3)
H26	0.9033	0.1607	0.7960	0.056*	0.899 (3)
Br3	0.8608 (7)	0.21715 (19)	0.3838 (6)	0.054 (2)*	0.101 (3)
C21A	0.756 (6)	0.197 (3)	0.829 (2)	0.045*	0.101 (3)
C22A	0.668 (5)	0.219 (3)	0.747 (3)	0.062*	0.101 (3)
H22A	0.5867	0.2298	0.7806	0.075*	0.101 (3)
C23A	0.699 (4)	0.225 (2)	0.616 (2)	0.062*	0.101 (3)
H23A	0.6392	0.2402	0.5601	0.075*	0.101 (3)
C24A	0.818 (3)	0.2090 (17)	0.5660 (15)	0.062*	0.101 (3)
C25A	0.907 (4)	0.1867 (17)	0.6480 (18)	0.062*	0.101 (3)
H25A	0.9876	0.1758	0.6145	0.075*	0.101 (3)
C26A	0.875 (5)	0.181 (2)	0.7796 (19)	0.062*	0.101 (3)
H26A	0.9351	0.1654	0.8350	0.075*	0.101 (3)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0404 (17)	0.0260 (14)	0.0375 (18)	-0.0012 (12)	-0.0011 (14)	-0.0105 (13)
F1	0.103 (3)	0.0442 (17)	0.0428 (19)	-0.0128 (17)	0.0068 (19)	0.0091 (14)
F2	0.119 (3)	0.0427 (17)	0.063 (2)	-0.039 (2)	0.021 (2)	0.0051 (17)
F3	0.071 (3)	0.101 (3)	0.090 (3)	0.004 (2)	0.044 (2)	0.032 (3)
N1	0.0288 (17)	0.0241 (16)	0.0247 (18)	0.0042 (13)	-0.0028 (14)	-0.0010 (14)
N2	0.0241 (15)	0.0214 (15)	0.0255 (19)	0.0018 (12)	0.0019 (14)	0.0007 (14)
N3	0.0235 (16)	0.0197 (14)	0.0265 (19)	0.0033 (12)	-0.0003 (13)	-0.0010 (13)
N4	0.0333 (18)	0.0281 (16)	0.0258 (18)	-0.0022 (14)	0.0025 (15)	0.0023 (15)
N5	0.047 (2)	0.0229 (17)	0.031 (2)	0.0074 (15)	0.0066 (18)	0.0020 (16)
C1	0.0256 (19)	0.0257 (19)	0.024 (2)	0.0051 (15)	0.0029 (15)	-0.0009 (16)
C2	0.0203 (18)	0.0254 (18)	0.029 (2)	0.0001 (14)	-0.0008 (16)	0.0024 (16)
C3	0.0210 (17)	0.0277 (19)	0.029 (2)	0.0016 (14)	-0.0037 (16)	-0.0034 (17)
C4	0.027 (2)	0.0196 (18)	0.040 (2)	0.0005 (15)	-0.0060 (18)	-0.0055 (18)
C5	0.047 (2)	0.028 (2)	0.041 (3)	-0.0088 (18)	-0.003 (2)	0.002 (2)
C6	0.034 (2)	0.032 (2)	0.041 (3)	-0.0076 (18)	0.000 (2)	0.005 (2)
C7	0.071 (4)	0.041 (3)	0.050 (4)	-0.013 (3)	0.016 (3)	0.005 (3)
C8	0.027 (2)	0.031 (2)	0.026 (2)	0.0038 (16)	0.0029 (17)	-0.0034 (17)
C9	0.034 (2)	0.037 (2)	0.065 (4)	-0.0027 (19)	-0.006 (2)	0.019 (2)
C10	0.035 (2)	0.059 (3)	0.062 (4)	0.012 (2)	-0.008 (2)	0.018 (3)
C11	0.020 (2)	0.067 (3)	0.045 (3)	0.000 (2)	-0.009 (2)	-0.015 (3)
C12	0.033 (2)	0.044 (3)	0.058 (3)	-0.009 (2)	0.006 (2)	-0.012 (2)
C13	0.029 (2)	0.033 (2)	0.047 (3)	-0.0071 (18)	-0.001 (2)	0.000 (2)
Br1	0.0269 (2)	0.1078 (5)	0.0743 (4)	0.0028 (3)	-0.0111 (3)	-0.0396 (4)
O2	0.0328 (16)	0.0275 (14)	0.0410 (19)	-0.0115 (12)	-0.0019 (13)	-0.0060 (13)
F4	0.054 (2)	0.075 (2)	0.105 (3)	0.0289 (17)	0.040 (2)	0.035 (2)
F5	0.0513 (18)	0.0253 (13)	0.097 (3)	0.0075 (12)	-0.0090 (18)	-0.0024 (16)
F6	0.0541 (19)	0.0514 (17)	0.084 (3)	0.0087 (15)	-0.0318 (19)	-0.0024 (19)
N6	0.0182 (16)	0.0241 (16)	0.039 (2)	0.0027 (12)	-0.0038 (14)	-0.0013 (15)
N7	0.0238 (16)	0.0228 (15)	0.0317 (19)	-0.0017 (12)	-0.0012 (14)	-0.0055 (15)
N8	0.0236 (16)	0.0170 (14)	0.0306 (19)	-0.0037 (13)	0.0000 (13)	-0.0022 (13)

## supplementary materials

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N9	0.0234 (16)	0.0271 (16)	0.036 (2)	-0.0004 (13)	-0.0010 (15)	-0.0021 (16)
N10	0.0282 (18)	0.0223 (17)	0.045 (2)	-0.0005 (13)	-0.0071 (16)	-0.0066 (16)
C20	0.036 (2)	0.024 (2)	0.053 (3)	0.0041 (17)	0.004 (2)	0.006 (2)
C14	0.0235 (19)	0.0188 (18)	0.035 (2)	-0.0034 (14)	-0.0021 (16)	0.0006 (16)
C15	0.0263 (19)	0.0203 (17)	0.0227 (19)	0.0001 (14)	-0.0019 (16)	0.0032 (16)
C16	0.0223 (18)	0.0272 (19)	0.024 (2)	-0.0066 (15)	0.0011 (16)	-0.0003 (16)
C17	0.033 (2)	0.0238 (18)	0.0199 (19)	-0.0006 (16)	0.0032 (16)	-0.0034 (16)
C18	0.032 (2)	0.0179 (17)	0.036 (2)	-0.0016 (16)	-0.0008 (18)	0.0034 (17)
C19	0.031 (2)	0.028 (2)	0.028 (2)	0.0018 (16)	0.0023 (18)	0.0035 (18)
Br2	0.1629 (13)	0.0842 (6)	0.0300 (3)	-0.0488 (7)	-0.0104 (5)	0.0130 (4)
C21	0.044 (3)	0.019 (2)	0.030 (3)	-0.017 (2)	-0.012 (2)	-0.0023 (19)
C22	0.053 (4)	0.051 (4)	0.039 (3)	0.004 (3)	-0.011 (3)	0.008 (3)
C23	0.084 (5)	0.051 (4)	0.045 (4)	-0.008 (4)	-0.024 (4)	0.012 (3)
C24	0.087 (5)	0.043 (3)	0.023 (3)	-0.027 (3)	-0.007 (3)	0.000 (3)
C25	0.092 (6)	0.063 (4)	0.031 (3)	-0.010 (4)	0.006 (3)	-0.011 (3)
C26	0.065 (4)	0.046 (3)	0.028 (3)	0.001 (3)	-0.003 (3)	-0.004 (2)

### *Geometric parameters (Å, °)*

O1—C4	1.229 (5)	N6—H6N	0.902 (19)
F1—C7	1.331 (8)	N7—C15	1.339 (5)
F2—C7	1.319 (6)	N7—C16	1.364 (5)
F3—C7	1.334 (7)	N8—C16	1.373 (5)
N1—C2	1.344 (6)	N8—C17	1.396 (5)
N1—C1	1.446 (5)	N8—C14	1.464 (5)
N1—H1N	0.87 (2)	N9—C16	1.317 (5)
N2—C2	1.334 (6)	N9—C19	1.368 (5)
N2—C3	1.348 (5)	N10—C15	1.311 (5)
N3—C3	1.379 (5)	N10—H10A	0.89 (2)
N3—C4	1.403 (5)	N10—H10B	0.90 (2)
N3—C1	1.465 (5)	C20—C19	1.516 (6)
N4—C3	1.318 (6)	C14—C21	1.509 (5)
N4—C6	1.351 (6)	C14—C21A	1.591 (9)
N5—C2	1.331 (5)	C14—H14	0.9900
N5—H5A	0.895 (14)	C17—C18	1.433 (6)
N5—H5B	0.892 (14)	C18—C19	1.343 (6)
C1—C8	1.519 (6)	C18—H18	0.9400
C1—H1A	0.9900	Br2—C24	1.875 (3)
C4—C5	1.423 (7)	C21—C22	1.3900
C5—C6	1.347 (8)	C21—C26	1.3900
C5—H5	0.9400	C22—C23	1.3900
C6—C7	1.517 (7)	C22—H22	0.9400
C8—C9	1.377 (6)	C23—C24	1.3900
C8—C13	1.381 (6)	C23—H23	0.9400
C9—C10	1.387 (7)	C24—C25	1.3900
C9—H9	0.9400	C25—C26	1.3900
C10—C11	1.371 (8)	C25—H25	0.9400
C10—H10	0.9400	C26—H26	0.9400
C11—C12	1.361 (8)	Br3—C24A	1.921 (7)

C11—Br1	1.893 (4)	C21A—C22A	1.3900
C12—C13	1.383 (7)	C21A—C26A	1.3900
C12—H12	0.9400	C22A—C23A	1.3900
C13—H13	0.9400	C22A—H22A	0.9400
O2—C17	1.219 (5)	C23A—C24A	1.3900
F4—C20	1.316 (6)	C23A—H23A	0.9400
F5—C20	1.298 (5)	C24A—C25A	1.3900
F6—C20	1.341 (7)	C25A—C26A	1.3900
N6—C15	1.352 (5)	C25A—H25A	0.9400
N6—C14	1.439 (5)	C26A—H26A	0.9400
C2—N1—C1	115.8 (4)	F5—C20—F4	108.7 (4)
C2—N1—H1N	119 (3)	F5—C20—F6	107.1 (4)
C1—N1—H1N	123 (3)	F4—C20—F6	105.4 (4)
C2—N2—C3	117.5 (3)	F5—C20—C19	113.0 (4)
C3—N3—C4	123.9 (4)	F4—C20—C19	111.7 (4)
C3—N3—C1	116.3 (3)	F6—C20—C19	110.5 (4)
C4—N3—C1	119.7 (3)	N6—C14—N8	107.3 (3)
C3—N4—C6	116.3 (4)	N6—C14—C21	112.5 (4)
C2—N5—H5A	113 (3)	N8—C14—C21	112.0 (4)
C2—N5—H5B	126 (4)	N6—C14—C21A	112 (3)
H5A—N5—H5B	121 (5)	N8—C14—C21A	106 (2)
N1—C1—N3	106.2 (3)	C21—C14—C21A	7(2)
N1—C1—C8	112.7 (3)	N6—C14—H14	108.3
N3—C1—C8	109.8 (3)	N8—C14—H14	108.3
N1—C1—H1A	109.3	C21—C14—H14	108.3
N3—C1—H1A	109.3	C21A—C14—H14	114.4
C8—C1—H1A	109.3	N10—C15—N7	120.2 (3)
N5—C2—N2	119.8 (4)	N10—C15—N6	118.1 (3)
N5—C2—N1	118.1 (4)	N7—C15—N6	121.6 (3)
N2—C2—N1	122.0 (4)	N9—C16—N7	117.7 (3)
N4—C3—N2	119.2 (4)	N9—C16—N8	121.7 (3)
N4—C3—N3	120.7 (3)	N7—C16—N8	120.6 (3)
N2—C3—N3	120.0 (4)	O2—C17—N8	120.0 (4)
O1—C4—N3	119.7 (4)	O2—C17—C18	126.8 (4)
O1—C4—C5	127.3 (4)	N8—C17—C18	113.1 (3)
N3—C4—C5	113.0 (4)	C19—C18—C17	118.9 (4)
C6—C5—C4	119.0 (4)	C19—C18—H18	120.6
C6—C5—H5	120.5	C17—C18—H18	120.6
C4—C5—H5	120.5	C18—C19—N9	126.3 (4)
C5—C6—N4	126.3 (4)	C18—C19—C20	120.6 (4)
C5—C6—C7	120.9 (4)	N9—C19—C20	113.1 (4)
N4—C6—C7	112.8 (4)	C22—C21—C26	120.0
F2—C7—F1	107.1 (5)	C22—C21—C14	117.5 (3)
F2—C7—F3	107.7 (5)	C26—C21—C14	122.5 (3)
F1—C7—F3	106.2 (5)	C21—C22—C23	120.0
F2—C7—C6	112.7 (5)	C21—C22—H22	120.0
F1—C7—C6	112.1 (4)	C23—C22—H22	120.0
F3—C7—C6	110.8 (5)	C24—C23—C22	120.0
C9—C8—C13	118.0 (4)	C24—C23—H23	120.0

## supplementary materials

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C9—C8—C1	121.2 (4)	C22—C23—H23	120.0
C13—C8—C1	120.9 (4)	C23—C24—C25	120.0
C8—C9—C10	121.5 (4)	C23—C24—Br2	120.2 (2)
C8—C9—H9	119.2	C25—C24—Br2	119.7 (2)
C10—C9—H9	119.2	C24—C25—C26	120.0
C11—C10—C9	118.7 (5)	C24—C25—H25	120.0
C11—C10—H10	120.7	C26—C25—H25	120.0
C9—C10—H10	120.7	C25—C26—C21	120.0
C12—C11—C10	121.3 (4)	C25—C26—H26	120.0
C12—C11—Br1	118.9 (4)	C21—C26—H26	120.0
C10—C11—Br1	119.7 (4)	C22A—C21A—C26A	120.0
C11—C12—C13	119.3 (5)	C22A—C21A—C14	123 (3)
C11—C12—H12	120.4	C26A—C21A—C14	117 (3)
C13—C12—H12	120.4	C21A—C22A—C23A	120.0
C8—C13—C12	121.2 (5)	C21A—C22A—H22A	120.0
C8—C13—H13	119.4	C23A—C22A—H22A	120.0
C12—C13—H13	119.4	C24A—C23A—C22A	120.0
C15—N6—C14	117.9 (3)	C24A—C23A—H23A	120.0
C15—N6—H6N	112 (3)	C22A—C23A—H23A	120.0
C14—N6—H6N	128 (3)	C23A—C24A—C25A	120.0
C15—N7—C16	117.8 (3)	C23A—C24A—Br3	119.9 (4)
C16—N8—C17	124.2 (3)	C25A—C24A—Br3	120.0 (4)
C16—N8—C14	117.9 (3)	C26A—C25A—C24A	120.0
C17—N8—C14	117.0 (3)	C26A—C25A—H25A	120.0
C16—N9—C19	115.7 (3)	C24A—C25A—H25A	120.0
C15—N10—H10A	118 (3)	C25A—C26A—C21A	120.0
C15—N10—H10B	122 (3)	C25A—C26A—H26A	120.0
H10A—N10—H10B	119 (5)	C21A—C26A—H26A	120.0
C2—N1—C1—N3	49.4 (5)	C14—N6—C15—N10	160.7 (4)
C2—N1—C1—C8	-70.9 (5)	C14—N6—C15—N7	-22.5 (6)
C3—N3—C1—N1	-45.3 (4)	C19—N9—C16—N7	178.7 (4)
C4—N3—C1—N1	136.7 (4)	C19—N9—C16—N8	-0.3 (6)
C3—N3—C1—C8	76.9 (4)	C15—N7—C16—N9	-166.1 (4)
C4—N3—C1—C8	-101.0 (4)	C15—N7—C16—N8	12.9 (6)
C3—N2—C2—N5	163.1 (4)	C17—N8—C16—N9	1.2 (6)
C3—N2—C2—N1	-13.9 (6)	C14—N8—C16—N9	-167.5 (4)
C1—N1—C2—N5	160.7 (4)	C17—N8—C16—N7	-177.8 (4)
C1—N1—C2—N2	-22.3 (6)	C14—N8—C16—N7	13.5 (6)
C6—N4—C3—N2	170.1 (4)	C16—N8—C17—O2	-177.5 (4)
C6—N4—C3—N3	-8.0 (6)	C14—N8—C17—O2	-8.7 (6)
C2—N2—C3—N4	-160.4 (4)	C16—N8—C17—C18	-0.2 (6)
C2—N2—C3—N3	17.8 (5)	C14—N8—C17—C18	168.6 (4)
C4—N3—C3—N4	9.9 (6)	O2—C17—C18—C19	175.5 (4)
C1—N3—C3—N4	-167.9 (4)	N8—C17—C18—C19	-1.6 (6)
C4—N3—C3—N2	-168.2 (3)	C17—C18—C19—N9	2.6 (7)
C1—N3—C3—N2	13.9 (5)	C17—C18—C19—C20	-178.1 (4)
C3—N3—C4—O1	178.5 (4)	C16—N9—C19—C18	-1.6 (7)
C1—N3—C4—O1	-3.8 (6)	C16—N9—C19—C20	179.1 (4)
C3—N3—C4—C5	-3.8 (5)	F5—C20—C19—C18	-4.4 (7)

C1—N3—C4—C5	174.0 (4)	F4—C20—C19—C18	118.5 (5)
O1—C4—C5—C6	174.3 (4)	F6—C20—C19—C18	-124.5 (5)
N3—C4—C5—C6	-3.2 (6)	F5—C20—C19—N9	175.0 (4)
C4—C5—C6—N4	5.0 (8)	F4—C20—C19—N9	-62.1 (6)
C4—C5—C6—C7	-177.2 (5)	F6—C20—C19—N9	54.9 (5)
C3—N4—C6—C5	0.8 (7)	N6—C14—C21—C22	-56.3 (4)
C3—N4—C6—C7	-177.1 (4)	N8—C14—C21—C22	-177.3 (3)
C5—C6—C7—F2	4.5 (8)	C21A—C14—C21—C22	-147 (25)
N4—C6—C7—F2	-177.4 (5)	N6—C14—C21—C26	123.7 (4)
C5—C6—C7—F1	125.4 (5)	N8—C14—C21—C26	2.6 (5)
N4—C6—C7—F1	-56.6 (6)	C21A—C14—C21—C26	33 (24)
C5—C6—C7—F3	-116.3 (6)	C26—C21—C22—C23	0.0
N4—C6—C7—F3	61.8 (6)	C14—C21—C22—C23	180.0 (5)
N1—C1—C8—C9	160.8 (5)	C21—C22—C23—C24	0.0
N3—C1—C8—C9	42.5 (6)	C22—C23—C24—C25	0.0
N1—C1—C8—C13	-19.2 (6)	C22—C23—C24—Br2	-178.6 (3)
N3—C1—C8—C13	-137.5 (4)	C23—C24—C25—C26	0.0
C13—C8—C9—C10	1.3 (8)	Br2—C24—C25—C26	178.6 (3)
C1—C8—C9—C10	-178.7 (5)	C24—C25—C26—C21	0.0
C8—C9—C10—C11	0.1 (9)	C22—C21—C26—C25	0.0
C9—C10—C11—C12	-1.5 (9)	C14—C21—C26—C25	-180.0 (5)
C9—C10—C11—Br1	177.8 (5)	N6—C14—C21A—C22A	-66 (4)
C10—C11—C12—C13	1.4 (9)	N8—C14—C21A—C22A	177 (3)
Br1—C11—C12—C13	-177.9 (4)	C21—C14—C21A—C22A	26 (22)
C9—C8—C13—C12	-1.4 (8)	N6—C14—C21A—C26A	114 (3)
C1—C8—C13—C12	178.6 (5)	N8—C14—C21A—C26A	-3(4)
C11—C12—C13—C8	0.1 (8)	C21—C14—C21A—C26A	-154 (27)
C15—N6—C14—N8	44.6 (5)	C26A—C21A—C22A—C23A	0.0
C15—N6—C14—C21	-79.0 (5)	C14—C21A—C22A—C23A	-180 (6)
C15—N6—C14—C21A	-71 (2)	C21A—C22A—C23A—C24A	0.0
C16—N8—C14—N6	-40.1 (5)	C22A—C23A—C24A—C25A	0.0
C17—N8—C14—N6	150.4 (3)	C22A—C23A—C24A—Br3	179 (4)
C16—N8—C14—C21	83.9 (5)	C23A—C24A—C25A—C26A	0.0
C17—N8—C14—C21	-85.6 (5)	Br3—C24A—C25A—C26A	-179 (4)
C16—N8—C14—C21A	80 (3)	C24A—C25A—C26A—C21A	0.0
C17—N8—C14—C21A	-89 (3)	C22A—C21A—C26A—C25A	0.0
C16—N7—C15—N10	168.1 (4)	C14—C21A—C26A—C25A	180 (6)
C16—N7—C15—N6	-8.7 (6)		

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>
N1—H1N...N2 <sup>i</sup>	0.87 (2)	2.15 (2)	3.005 (5)	171 (5)
N5—H5A...O2 <sup>ii</sup>	0.895 (14)	2.09 (3)	2.905 (5)	152 (5)
N5—H5B...N4 <sup>i</sup>	0.892 (14)	2.25 (2)	3.095 (6)	159 (5)
N5—H5B...F1 <sup>i</sup>	0.892 (14)	2.46 (4)	3.054 (5)	124 (4)
N6—H6N...N7 <sup>iii</sup>	0.902 (19)	2.10 (3)	2.967 (5)	160 (5)
N10—H10A...O1	0.89 (2)	2.03 (3)	2.885 (5)	162 (5)

# supplementary materials

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N10—H10B···N9<sup>iii</sup>

0.90 (2)

2.15 (2)

3.041 (5)

171 (5)

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

Fig. 1

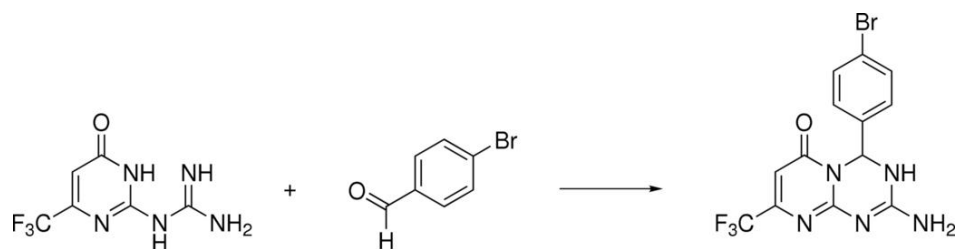


Fig. 2

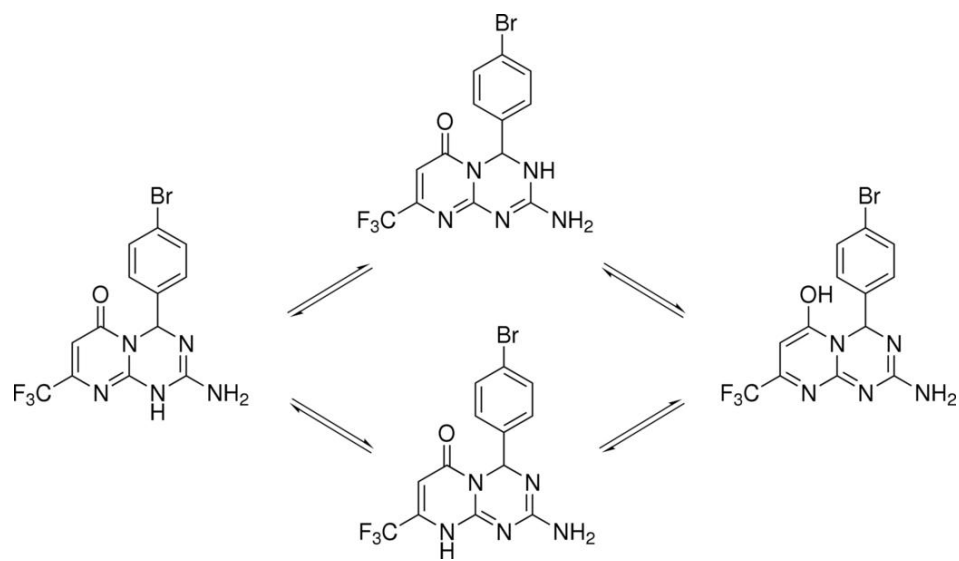


Fig. 3

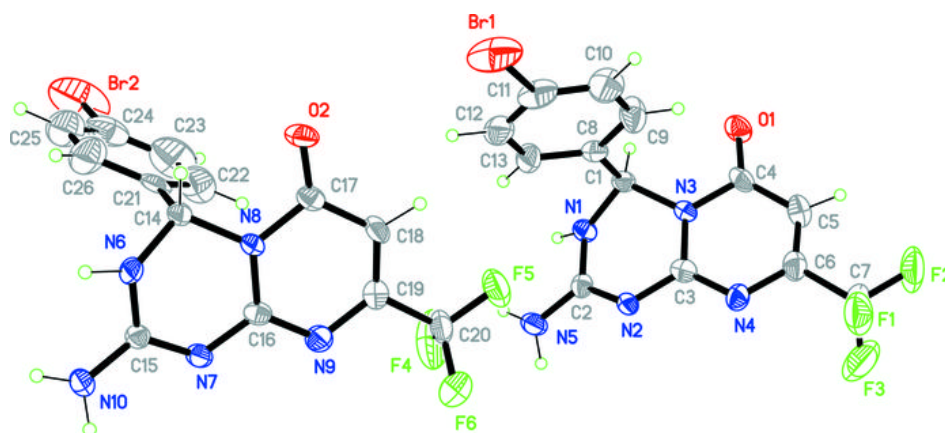


Fig. 4

