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Methyl 7-(4-bromophenyl)-5-methyl-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-6-carboxylate

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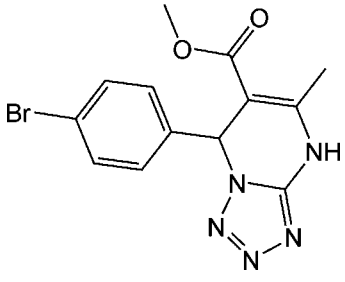
Key indicators: single-crystal X-ray study; T = 113 K; mean σ(C–C) = 0.003 Å; R factor = 0.035; wR factor = 0.083; data-to-parameter ratio = 16.6.

The title compound, $C_{13}H_{12}BrN_5O_2$, was obtained by the solid-state reaction of 4-bromobenzaldehyde, 1*H*-tetrazol-5-amine hydrate and methyl acetoacetate catalysed by sulfamic acid. The pyrimidine ring adopts a flattened boat conformation. In the crystal structure, centrosymmetrically related molecules are linked into dimers by intermolecular N—H···N hydrogen bonds.

Related literature

For the biological activities of dihydrotetrazolo[1,5-*a*]-pyrimidines, see: Ali (2006); Ismail *et al.* (2002); Lansbury & Liu (2006).



Experimental

Crystal data

$C_{13}H_{12}BrN_5O_2$
M_r = 350.19
Monoclinic, $P2_1/c$
a = 17.907 (2) Å
b = 10.1825 (12) Å
c = 7.5055 (8) Å
β = 92.166 (6)°
V = 1367.6 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.02 mm^{-1}
T = 113 (2) K
0.16 × 0.14 × 0.10 mm

Data collection

Rigaku Saturn diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2002)
T_{min} = 0.644, T_{max} = 0.752
10315 measured reflections
3261 independent reflections
2480 reflections with $I > 2\sigma(I)$
R_{int} = 0.054

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.083
S = 0.99
3261 reflections
196 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.98 e Å^{-3}
$\Delta\rho_{min}$ = −1.14 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5···N4^{i}	0.90 (3)	1.98 (3)	2.851 (3)	164 (3)

Symmetry code: (i) $-x+1, -y, -z+1$.

Data collection: *CrystalClear* (Rigaku/MSC, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2436).

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supplementary materials

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Methyl 7-(4-bromophenyl)-5-methyl-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-6-carboxylate

C.-S. Yao, C.-X. Yu, L. Song and S.-J. Tu

Comment

As the analogs of purine, the derivatives of dihydrotetrazolo[1,5-*a*] pyrimidine are reported to have various biological activities, such as antimicrobial (Ali, 2006), farnesyl transferase inhibitory (Lansbury & Liu, 2006), antihypertensive (Ismail *et al.*, 2002) acrivities, *etc*. This led us to pay more attention to the synthesis and structure determination of these compounds. To further study the relationship between the structure and bioactivity, we synthesized a series of dihydrotetrazolo[1,5-*a*]pyrimidine derivatives. We report here the crystal structure of the title compound.

The molecular structure of the title compound is shown in Fig. 1. The pyrimidine ring adopts a flattened-boat conformation, with atoms N5 and C1 deviating from the N1/C2/C3/C4 plane by 0.118 (4) Å and 0.175 (4) Å, respectively. The N1—N4/C2 and C5—C10 planes form dihedral angles of 9.56 (17)° and 86.95 (7)°, respectively, with the N1/C2/C3/C4 plane.

In the crystal structure, inversion-related molecules are linked to form a dimer by N—H···N hydrogen bonds (Fig.2 and Table 2).

Experimental

The title compound was synthesized by solid-state reaction of 4-bromobenzaldehyde, 1*H*-tetrazol-5-amine hydrate and methyl acetoacetate in a 1:1:1 molar ratio, catalyzed by sulfamic acid at 363 K. After cooling, the reaction mixture was washed with water and recrystallized from ethanol, giving single crystals suitable for X-ray diffraction.

Refinement

The H atom bonded to a N atom was located in a difference map and was refined freely. Other H atoms were placed in calculated positions, with C—H = 0.95–1.00 Å, and included in the final cycles of refinement using a riding model, with U_{iso}(H) = 1.2–1.5U_{eq}(parent atom).

Figures

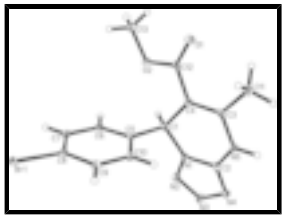

Fig. 1. The molecular structure of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme.

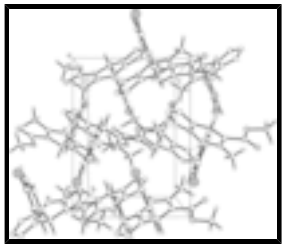

Fig. 2. The packing diagram of the title compound. Intermolecular hydrogen bonds are shown as dashed lines.

Methyl 7-(4-bromophenyl)-5-methyl-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine- 6-carboxylate

Crystal data

$C_{13}H_{12}BrN_5O_2$	F_{000} = 704
M_r = 350.19	D_x = 1.701 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71070 Å
Hall symbol: -P 2ybc	Cell parameters from 3874 reflections
a = 17.907 (2) Å	θ = 2.3–27.9º
b = 10.1825 (12) Å	μ = 3.02 mm^{-1}
c = 7.5055 (8) Å	T = 113 (2) K
β = 92.166 (6)º	Prism, colourless
V = 1367.6 (3) Å^3	0.16 × 0.14 × 0.10 mm
Z = 4	

Data collection

Rigaku Saturn diffractometer	3261 independent reflections
Radiation source: rotating anode	2480 reflections with $I > 2\sigma(I)$
Monochromator: confocal	R_{int} = 0.054
T = 113(2) K	θ_{max} = 27.9º
ω scans	θ_{min} = 2.3º
Absorption correction: multi-scan (CrystalClear; Rigaku/MSC, 2002)	h = −23→22
T_{min} = 0.644, T_{max} = 0.752	k = −13→11
10315 measured reflections	l = −9→8

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.035	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.083	$w = 1/[\sigma^2(F_o^2) + (0.0433P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 0.99	$(\Delta/\sigma)_{max}$ = 0.001
3261 reflections	$\Delta\rho_{max}$ = 0.98 e Å^{-3}

196 parameters

Primary atom site location: structure-invariant direct methods

$\Delta\rho_{min} = -1.14$ e Å^{-3}

Extinction correction: none

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.004726 (12)	0.27862 (2)	0.46614 (4)	0.02132 (10)
O1	0.29676 (9)	0.06840 (16)	−0.1887 (2)	0.0220 (4)
O2	0.21121 (9)	−0.05636 (16)	−0.0569 (2)	0.0180 (4)
N1	0.32618 (9)	−0.09411 (17)	0.4092 (3)	0.0127 (4)
N2	0.31537 (10)	−0.17956 (19)	0.5438 (3)	0.0176 (4)
N3	0.37654 (10)	−0.1804 (2)	0.6404 (3)	0.0202 (5)
N4	0.42826 (10)	−0.09703 (19)	0.5731 (3)	0.0175 (4)
N5	0.42234 (11)	0.0382 (2)	0.3083 (3)	0.0184 (4)
C1	0.27228 (12)	−0.0655 (2)	0.2624 (3)	0.0132 (5)
H1	0.2521	−0.1504	0.2140	0.016*
C2	0.39545 (12)	−0.0462 (2)	0.4286 (3)	0.0146 (5)
C3	0.38423 (13)	0.0551 (2)	0.1451 (3)	0.0153 (5)
C4	0.31497 (12)	0.0029 (2)	0.1174 (3)	0.0141 (5)
C5	0.20761 (12)	0.0163 (2)	0.3260 (3)	0.0131 (5)
C6	0.13503 (13)	−0.0321 (2)	0.3065 (3)	0.0153 (5)
H6	0.1270	−0.1185	0.2622	0.018*
C7	0.07433 (12)	0.0442 (2)	0.3509 (3)	0.0172 (5)
H7	0.0248	0.0115	0.3353	0.021*
C8	0.08719 (12)	0.1684 (2)	0.4182 (3)	0.0157 (5)
C9	0.15873 (12)	0.2177 (2)	0.4453 (4)	0.0172 (5)
H9	0.1665	0.3025	0.4954	0.021*
C10	0.21876 (12)	0.1413 (2)	0.3980 (3)	0.0158 (5)
H10	0.2681	0.1743	0.4149	0.019*
C11	0.42716 (13)	0.1333 (3)	0.0139 (4)	0.0245 (6)
H11A	0.4271	0.0866	−0.1003	0.037*
H11B	0.4787	0.1448	0.0596	0.037*
H11C	0.4037	0.2195	−0.0033	0.037*
C12	0.27653 (13)	0.0108 (2)	−0.0590 (3)	0.0155 (5)
C13	0.16691 (13)	−0.0577 (3)	−0.2211 (3)	0.0209 (5)
H13A	0.1594	0.0326	−0.2635	0.031*

H13B	0.1183	−0.0981	−0.2007	0.031*
H13C	0.1929	−0.1084	−0.3109	0.031*
H5	0.4699 (16)	0.065 (3)	0.325 (4)	0.030 (8)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01894 (14)	0.02864 (16)	0.01634 (16)	0.00961 (10)	0.00019 (10)	−0.00313 (10)
O1	0.0226 (9)	0.0263 (9)	0.0171 (10)	−0.0007 (7)	0.0014 (8)	0.0043 (8)
O2	0.0168 (8)	0.0252 (9)	0.0118 (9)	−0.0009 (7)	−0.0027 (7)	0.0017 (7)
N1	0.0120 (8)	0.0137 (9)	0.0125 (11)	−0.0016 (7)	0.0012 (8)	0.0022 (8)
N2	0.0165 (9)	0.0195 (10)	0.0168 (12)	−0.0015 (8)	−0.0003 (9)	0.0051 (9)
N3	0.0151 (9)	0.0243 (10)	0.0210 (12)	−0.0021 (8)	−0.0022 (9)	0.0065 (9)
N4	0.0141 (9)	0.0211 (10)	0.0172 (11)	−0.0009 (8)	−0.0003 (8)	0.0057 (9)
N5	0.0127 (9)	0.0230 (10)	0.0194 (12)	−0.0057 (8)	−0.0019 (9)	0.0059 (9)
C1	0.0112 (10)	0.0140 (11)	0.0143 (12)	−0.0009 (8)	−0.0017 (9)	0.0012 (9)
C2	0.0114 (10)	0.0147 (10)	0.0179 (13)	−0.0009 (8)	0.0011 (9)	0.0004 (10)
C3	0.0162 (10)	0.0148 (11)	0.0151 (13)	0.0017 (9)	0.0027 (10)	0.0012 (9)
C4	0.0153 (10)	0.0139 (11)	0.0133 (13)	0.0032 (8)	0.0021 (10)	0.0015 (9)
C5	0.0133 (10)	0.0171 (11)	0.0090 (12)	0.0002 (8)	0.0003 (9)	0.0015 (9)
C6	0.0150 (10)	0.0159 (11)	0.0148 (13)	−0.0025 (9)	−0.0009 (10)	−0.0019 (10)
C7	0.0127 (10)	0.0239 (12)	0.0149 (13)	−0.0032 (9)	−0.0016 (10)	0.0018 (10)
C8	0.0151 (10)	0.0192 (11)	0.0129 (12)	0.0054 (9)	0.0015 (9)	0.0027 (10)
C9	0.0194 (11)	0.0143 (11)	0.0178 (14)	−0.0016 (9)	−0.0001 (10)	0.0000 (10)
C10	0.0136 (10)	0.0168 (11)	0.0168 (13)	−0.0014 (9)	−0.0015 (10)	0.0009 (9)
C11	0.0181 (11)	0.0326 (14)	0.0230 (15)	−0.0031 (10)	0.0026 (11)	0.0111 (12)
C12	0.0152 (10)	0.0152 (11)	0.0162 (13)	0.0031 (9)	0.0033 (10)	−0.0012 (9)
C13	0.0184 (11)	0.0304 (13)	0.0137 (13)	0.0011 (10)	−0.0041 (10)	0.0002 (11)

Geometric parameters (Å, °)

Br1—C8	1.900 (2)	C4—C12	1.471 (3)
O1—C12	1.204 (3)	C5—C6	1.393 (3)
O2—C12	1.356 (3)	C5—C10	1.394 (3)
O2—C13	1.441 (3)	C6—C7	1.387 (3)
N1—C2	1.336 (3)	C6—H6	0.95
N1—N2	1.353 (3)	C7—C8	1.377 (3)
N1—C1	1.466 (3)	C7—H7	0.95
N2—N3	1.291 (3)	C8—C9	1.384 (3)
N3—N4	1.367 (3)	C9—C10	1.384 (3)
N4—C2	1.320 (3)	C9—H9	0.95
N5—C2	1.348 (3)	C10—H10	0.95
N5—C3	1.390 (3)	C11—H11A	0.98
N5—H5	0.90 (3)	C11—H11B	0.98
C1—C5	1.518 (3)	C11—H11C	0.98
C1—C4	1.522 (3)	C13—H13A	0.98
C1—H1	1.00	C13—H13B	0.98
C3—C4	1.358 (3)	C13—H13C	0.98
C3—C11	1.500 (3)		

C12—O2—C13	116.22 (19)	C7—C6—H6	119.6
C2—N1—N2	108.20 (18)	C5—C6—H6	119.6
C2—N1—C1	126.2 (2)	C8—C7—C6	118.7 (2)
N2—N1—C1	125.47 (17)	C8—C7—H7	120.6
N3—N2—N1	106.34 (18)	C6—C7—H7	120.6
N2—N3—N4	111.16 (19)	C7—C8—C9	121.9 (2)
C2—N4—N3	105.10 (17)	C7—C8—Br1	119.42 (16)
C2—N5—C3	119.55 (19)	C9—C8—Br1	118.66 (17)
C2—N5—H5	117.4 (18)	C8—C9—C10	118.8 (2)
C3—N5—H5	121.2 (19)	C8—C9—H9	120.6
N1—C1—C5	111.18 (19)	C10—C9—H9	120.6
N1—C1—C4	107.10 (17)	C9—C10—C5	120.8 (2)
C5—C1—C4	112.55 (18)	C9—C10—H10	119.6
N1—C1—H1	108.6	C5—C10—H10	119.6
C5—C1—H1	108.6	C3—C11—H11A	109.5
C4—C1—H1	108.6	C3—C11—H11B	109.5
N4—C2—N1	109.2 (2)	H11A—C11—H11B	109.5
N4—C2—N5	129.9 (2)	C3—C11—H11C	109.5
N1—C2—N5	120.9 (2)	H11A—C11—H11C	109.5
C4—C3—N5	120.1 (2)	H11B—C11—H11C	109.5
C4—C3—C11	126.5 (2)	O1—C12—O2	122.8 (2)
N5—C3—C11	113.41 (19)	O1—C12—C4	127.5 (2)
C3—C4—C12	120.6 (2)	O2—C12—C4	109.6 (2)
C3—C4—C1	123.4 (2)	O2—C13—H13A	109.5
C12—C4—C1	115.98 (19)	O2—C13—H13B	109.5
C6—C5—C10	118.9 (2)	H13A—C13—H13B	109.5
C6—C5—C1	119.54 (19)	O2—C13—H13C	109.5
C10—C5—C1	121.53 (19)	H13A—C13—H13C	109.5
C7—C6—C5	120.9 (2)	H13B—C13—H13C	109.5
C2—N1—N2—N3	0.7 (3)	C5—C1—C4—C3	107.3 (2)
C1—N1—N2—N3	177.5 (2)	N1—C1—C4—C12	165.17 (18)
N1—N2—N3—N4	0.0 (3)	C5—C1—C4—C12	−72.3 (2)
N2—N3—N4—C2	−0.6 (3)	N1—C1—C5—C6	−120.8 (2)
C2—N1—C1—C5	−110.9 (3)	C4—C1—C5—C6	119.0 (2)
N2—N1—C1—C5	72.9 (3)	N1—C1—C5—C10	61.5 (3)
C2—N1—C1—C4	12.4 (3)	C4—C1—C5—C10	−58.7 (3)
N2—N1—C1—C4	−163.8 (2)	C10—C5—C6—C7	2.6 (4)
N3—N4—C2—N1	1.1 (3)	C1—C5—C6—C7	−175.2 (2)
N3—N4—C2—N5	−177.4 (3)	C5—C6—C7—C8	−1.2 (4)
N2—N1—C2—N4	−1.1 (3)	C6—C7—C8—C9	−1.2 (4)
C1—N1—C2—N4	−177.9 (2)	C6—C7—C8—Br1	176.14 (18)
N2—N1—C2—N5	177.5 (2)	C7—C8—C9—C10	2.1 (4)
C1—N1—C2—N5	0.7 (4)	Br1—C8—C9—C10	−175.25 (19)
C3—N5—C2—N4	165.1 (2)	C8—C9—C10—C5	−0.6 (4)
C3—N5—C2—N1	−13.2 (4)	C6—C5—C10—C9	−1.7 (4)
C2—N5—C3—C4	10.0 (4)	C1—C5—C10—C9	176.1 (2)
C2—N5—C3—C11	−170.0 (2)	C13—O2—C12—O1	1.1 (3)
N5—C3—C4—C12	−175.0 (2)	C13—O2—C12—C4	−179.99 (18)

C11—C3—C4—C12	5.0 (4)	C3—C4—C12—O1	−5.7 (4)
N5—C3—C4—C1	5.4 (4)	C1—C4—C12—O1	173.9 (2)
C11—C3—C4—C1	−174.6 (2)	C3—C4—C12—O2	175.5 (2)
N1—C1—C4—C3	−15.2 (3)	C1—C4—C12—O2	−4.9 (3)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5···N4^{i}	0.90 (3)	1.98 (3)	2.851 (3)	164 (3)

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1.

Fig. 1

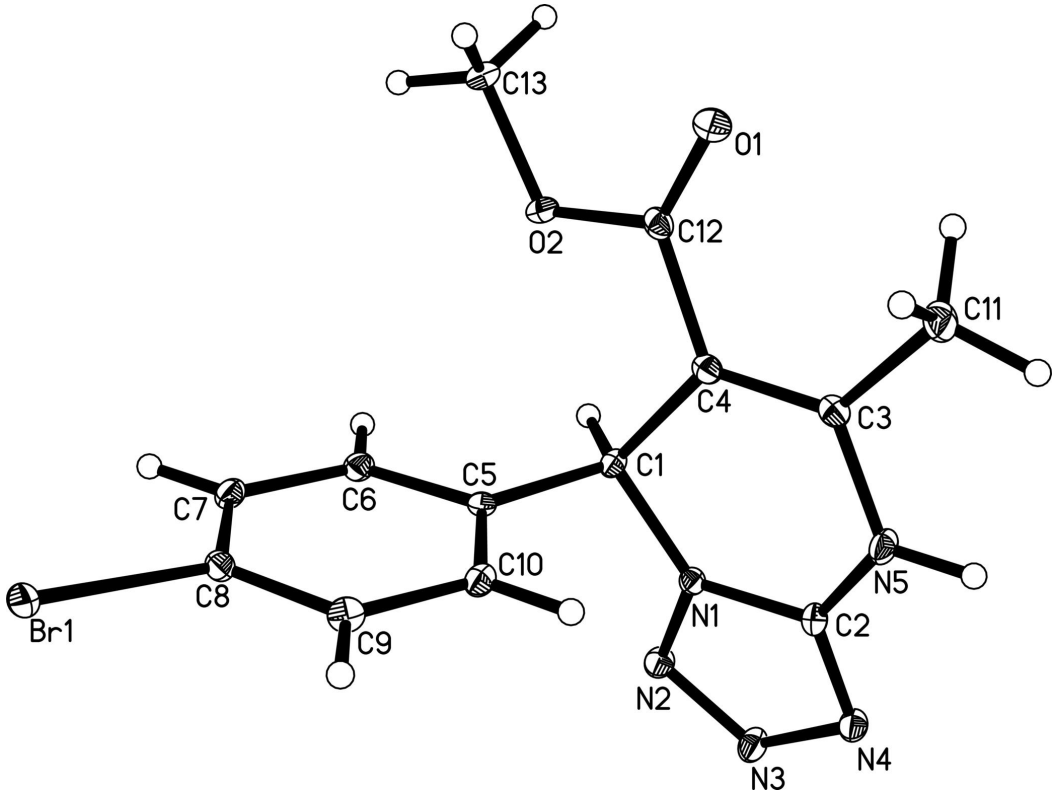

Fig. 2