

3-Bromo-7-methoxy-2-(tetrahydropyran-2-yl)-pyrazolo[4,3-*d*]pyrimidine

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In the title compound, $C_{11}H_{13}BrN_4O_2$, the pyrimidine and pyrazole rings make a dihedral angle of $3.8(6)^\circ$. The pendant tetrahydropyran ring is in a chair conformation and its mean plane makes an interplanar angle of $52.5(6)^\circ$ with the pyrazole ring. There is a short $Br \cdots O$ intermolecular contact of $2.994(7) \text{ \AA}$.

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Key indicators

Single-crystal X-ray study

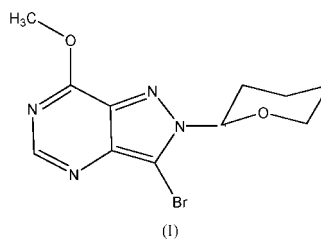
 $T = 163 \text{ K}$ Mean $\sigma(C-C) = 0.015 \text{ \AA}$ R factor = 0.059 wR factor = 0.147

Data-to-parameter ratio = 12.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Comment

The title compound, (I), was studied in order to confirm the regioselectivity, based on ^{13}C NMR, of the critical tetrahydropyranyl-protecting group. The crystal structure is built of isolated molecules (Fig. 1) and only weak intermolecular contacts *e.g.* $C5-H5 \cdots O2^i$ [symmetry code: (i) $x - 1/2, 3/2 - y, z$] with $C5 \cdots O2^i = 3.29(1) \text{ \AA}$. There is also a short intermolecular contact between Br1 and $O1^{ii}$ of $2.994(7) \text{ \AA}$ [symmetry code: (ii) $-x, 1 - y, z - 1/2$]. A search of the Cambridge Structural Database (Allen & Kennard, 1993; CCDC, 2002a) gives the (closest) similar interaction of 3.024 \AA in 5-bromo-11-ethylenedioxy-5-nitro-2-oxapentacyclo[7.3.0^{3,7}.O^{4,12}O^{6,11}]dodecane (Watson *et al.*, 1990) and, interestingly, this is the only interaction between the molecules in one direction in the lattice (CCDC, 2002b). Two other short $Br \cdots O$ intermolecular distances have been reported, *viz.* 3.094 (Gu *et al.*, 1986) and 3.102 \AA (Tomilov *et al.*, 1999), but in these latter cases there are further intermolecular contacts between the same pairs of molecules. There is also one close intramolecular interaction here, *viz.* $C1'-H1' \cdots Br1$ with $C1' \cdots Br1 = 3.27(1) \text{ \AA}$.



The $C-Br$ distance is $1.85(1) \text{ \AA}$, identical to that in 4-bromo-3-(3-pyridyl)sydnone (Hašek *et al.*, 1979); $C-Br$ bond distances from sp^2 -hybridized C atoms lie in the range $1.793-1.932 \text{ \AA}$ (CCDC, 2002a). The fused five- and six-membered rings are each planar, with average deviations of $0.008(6)$ and $0.007(7) \text{ \AA}$, respectively; their least-squares planes form a dihedral angle of $3.8(6)^\circ$. The pendant tetrahydropyran ring ($O1/C1'-C5'$) is in a chair conformation [$Q = 0.57(1) \text{ \AA}$ and $\theta = 3.4(12)^\circ$; Boeyens, 1978] and the mean plane through this ring makes an angle of $52.5(6)^\circ$ with the pyrazole ring.

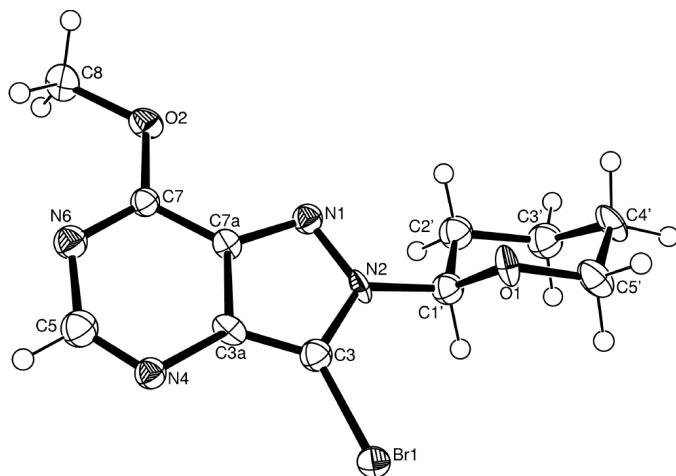


Figure 1
The molecular structure of (I) (Farrugia, 1997). Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The title compound was prepared as described by Stone *et al.* (1979) and recrystallized from methanol.

Crystal data

$C_{11}H_{13}BrN_4O_2$
 $M_r = 313.16$
Orthorhombic, $Pna2_1$
 $a = 12.4224$ (4) Å
 $b = 17.1489$ (5) Å
 $c = 5.6680$ (1) Å
 $V = 1207.46$ (6) Å³
 $Z = 4$
 $D_x = 1.723$ Mg m⁻³

Mo $K\alpha$ radiation
Cell parameters from 2337 reflections
 $\theta = 2.9\text{--}25.8^\circ$
 $\mu = 3.41$ mm⁻¹
 $T = 163$ (2) K
Needle, pale yellow
 $0.50 \times 0.06 \times 0.04$ mm

Data collection

Bruker P4 diffractometer
 ω scans
Absorption correction: multi-scan (Blessing, 1995)
 $T_{\min} = 0.290$, $T_{\max} = 0.876$
3279 measured reflections
1475 independent reflections

1188 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.058$
 $\theta_{\text{max}} = 26.1^\circ$
 $h = -12 \rightarrow 12$
 $k = -14 \rightarrow 21$
 $l = -7 \rightarrow 6$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.059$
 $wR(F^2) = 0.147$
 $S = 0.99$
1475 reflections
117 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0903P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.00$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.45$ e Å⁻³
Absolute structure: (Flack, 1983),
161 Friedel pairs
Flack parameter = 0.00 (3)

Table 1

Selected geometric parameters (Å, °).

Br1—C3	1.850 (10)	N4—C5	1.251 (12)
N1—N2	1.343 (11)	N6—C7	1.315 (14)
N1—C7A	1.360 (12)	C3—C3A	1.344 (15)
N2—N1—C7A	103.6 (8)	N1—N2—C1'	120.9 (9)
Br1—C3—C3A—N4	−3.9 (18)	N1—N2—C1'—O1	102.2 (10)

The *_measured_fraction_theta_max* was low (0.76), resulting from a collection algorithm limit error with the maximum h index 12 instead of 15. The data-to-parameter ratio and Flack (1983) parameter s.u. are adequate, and atoms N1, N4, N6, C3, C5, C7, C1, C2 and C3 could only be refined with isotropic displacement parameters. All H atoms were included in the riding-model approximation with an isotropic displacement parameter constrained to 1.2 times that of the U_{eq} value of their parent atom (SHELXL97; Sheldrick, 1997). The maximum and minimum residual electron-density peaks are 0.06 and 1.00 Å⁻³ from atom Br1.

Data collection: SMART (Siemens, 1996); cell refinement: SMART; data reduction: SAINT (Siemens, 1996) and SADABS (Sheldrick, 1996); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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