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7-Bromo-1,4-bis(prop-2-ynyl)pyrido[2,3-*b*]-pyrazine-2,3(1*H*,4*H*)-dione

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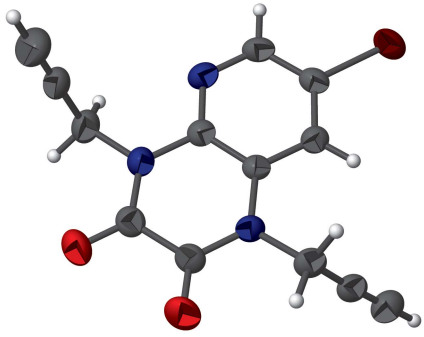
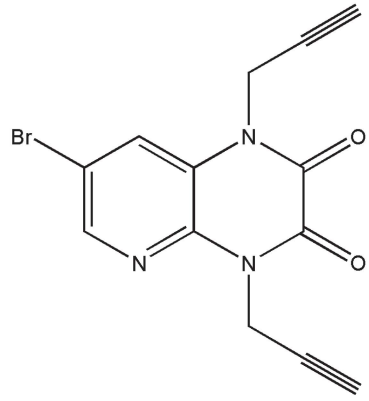
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{13}H_8BrN_3O_2$, the pyrido-pyrazine fused-ring system is essentially planar (r.m.s. deviation = 0.061 Å). The prop-2-ynyl moieties are twisted away from the ring system in opposite directions. In the crystal, a single weak C—H···O interaction generates [010] chains and aromatic π–π stacking interactions between the pyridine rings are observed.

3D view



Chemical scheme



Structure description

Heterocycles containing a pyrido-pyrazine grouping possess useful medicinal properties (Zhang *et al.*, 2012). They may also exhibit good inhibitory action on the corrosion of metals (Ouzidan *et al.*, 2016). As part of our studies in this area, we now report the synthesis of a new pyrido[2,3-*b*]pyrazine and its crystal structure.

The title compound crystallizes with one molecule in the asymmetric unit (Fig. 1). The pyrido-pyrazine moiety is essentially planar: the dihedral angle between the fused rings is 4.7 (6)°. The prop-2-ynyl moieties are twisted away from the mean plane of the pyrido-pyrazine ring [C8—C9—N2 = 114.0 (2)° and C12—C11—N1 = 110.1 (3)°] to avoid steric repulsion. In the crystal, a single weak C6—H6···O2 interaction links the molecules into [010] chains (Fig. 2 and Table 1). In addition, weak π–π stacking between the pyridine rings is observed [centroid–centroid separation = 3.7089 (2) Å].

Synthesis and crystallization

To a solution of 7-bromopyrido[2,3-*b*]pyrazine-2,3(1*H*,4*H*)-dione (0.2 g, 0.826 mmol), K_2CO_3 (0.456 g, 3.304 mmol), tetra-*n*-bromide butyl ammonium (0.1 mmol) in DMF (15 ml) was added propargyl bromide (0.213 ml, 1.790 mmol), and the mixture was stirred for 24 h at room temperature. After the solvent was evaporated under reduced pressure,

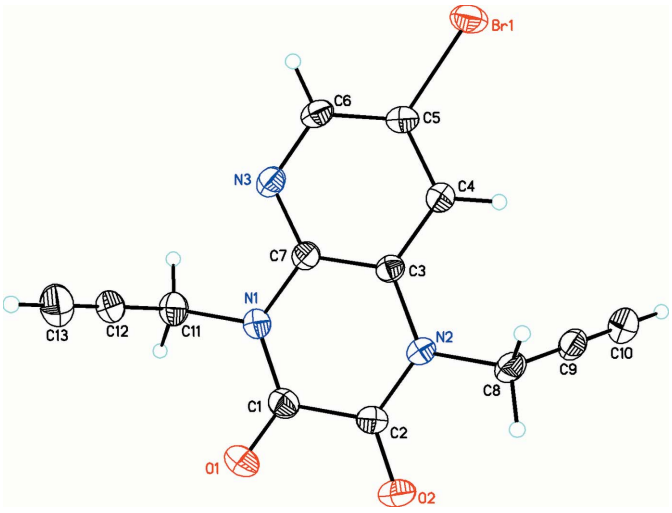


Figure 1
A view of the molecular structure, showing displacement ellipsoids drawn at the 30% probability level.

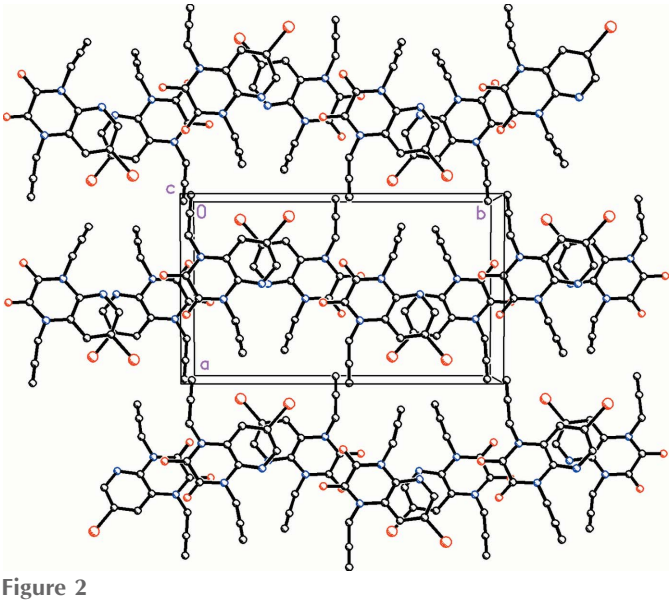


Figure 2
A partial view along the *c* axis of the crystal packing. All H atoms except H6 have been omitted for clarity.

the product was isolated by chromatography on a silica gel column with ethyl acetate/hexane (1 /3) as the eluent. Red crystals were isolated when the solvent was allowed to evaporate (yield = 18%, m.p. 449 K).

Refinement

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

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

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···O2^{i}	0.93	2.58	3.326 (4)	137

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{13}H_8BrN_3O_2$
M_r	318.13
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	10.1922 (5), 17.347 (1), 7.0216 (4)
β (°)	92.382 (5)
V (Å^3)	1240.38 (12)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	4.55
Crystal size (mm)	0.22 × 0.16 × 0.1
Data collection	
Diffractometer	Rigaku Oxford Diffraction
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.428, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4477, 2361, 1994
R_{int}	0.025
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.614
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.101, 1.06
No. of reflections	2361
No. of parameters	172
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.50, −0.43

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

Funding information

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full crystallographic data

IUCrData (2018). **3**, x180266 [https://doi.org/10.1107/S2414314618002663]

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Crystal data

$C_{13}H_8BrN_3O_2$
M_r = 318.13
Monoclinic, $P2_1/c$
a = 10.1922 (5) Å
b = 17.347 (1) Å
c = 7.0216 (4) Å
β = 92.382 (5)°
V = 1240.38 (12) Å^3
Z = 4
$F(000)$ = 632
D_x = 1.704 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 1740 reflections
θ = 4.3–71.4°
μ = 4.55 mm^{-1}
T = 293 K
Prism, red
0.22 × 0.16 × 0.1 mm

Data collection

Rigaku Oxford Diffraction model name? diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Cu) X-ray Source
Graphite monochromator
Detector resolution: 16.0416 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2015)
T_{min} = 0.428, T_{max} = 1.000
4477 measured reflections
2361 independent reflections
1994 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 71.3°, θ_{min} = 4.3°
h = −12→9
k = −20→18
l = −8→7

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.101
S = 1.06
2361 reflections
172 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 0.1537P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

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.

Refinement. All the H atoms were placed in their calculated positions and then refined using a riding model with bond lengths of 0.93 Å (CH) or 0.97 Å (CH2). Isotropic displacement parameters for all these atoms were set to 1.2 (CH, CH2) times U_{eq} of the parent atom.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.11401 (3)	0.16664 (2)	0.36163 (5)	0.05288 (15)
O1	0.6397 (2)	0.49748 (14)	0.1531 (4)	0.0559 (6)
O2	0.4267 (3)	0.56084 (13)	0.3097 (4)	0.0620 (7)
N1	0.5551 (2)	0.37741 (14)	0.1875 (3)	0.0396 (5)
N2	0.3293 (2)	0.44352 (13)	0.3284 (3)	0.0363 (5)
N3	0.4718 (2)	0.25464 (14)	0.2338 (3)	0.0402 (5)
C1	0.5508 (3)	0.45577 (17)	0.2002 (4)	0.0416 (6)
C2	0.4292 (3)	0.49169 (17)	0.2831 (4)	0.0419 (6)
C3	0.3366 (2)	0.36362 (15)	0.3063 (4)	0.0325 (5)
C4	0.2339 (3)	0.31484 (16)	0.3433 (4)	0.0370 (5)
H4	0.1537	0.3342	0.3800	0.044*
C5	0.2537 (3)	0.23636 (15)	0.3243 (4)	0.0373 (5)
C6	0.3740 (3)	0.20755 (16)	0.2754 (4)	0.0411 (6)
H6	0.3869	0.1545	0.2715	0.049*
C7	0.4528 (3)	0.32983 (15)	0.2449 (4)	0.0347 (5)
C8	0.2161 (3)	0.47795 (16)	0.4219 (4)	0.0422 (6)
H8A	0.2010	0.4495	0.5379	0.051*
H8B	0.2379	0.5306	0.4578	0.051*
C9	0.0952 (3)	0.47845 (17)	0.3036 (5)	0.0436 (6)
C10	−0.0066 (3)	0.4782 (2)	0.2184 (5)	0.0535 (8)
H10	−0.0871	0.4780	0.1511	0.064*
C11	0.6748 (3)	0.34154 (19)	0.1177 (5)	0.0507 (7)
H11A	0.6521	0.2944	0.0499	0.061*
H11B	0.7160	0.3762	0.0297	0.061*
C12	0.7673 (3)	0.32418 (18)	0.2785 (6)	0.0524 (8)
C13	0.8389 (4)	0.3114 (3)	0.4095 (7)	0.0715 (11)
H13	0.8958	0.3012	0.5135	0.086*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0547 (2)	0.0393 (2)	0.0645 (2)	−0.01276 (13)	0.00117 (15)	0.00276 (13)
O1	0.0480 (12)	0.0521 (13)	0.0681 (15)	−0.0138 (10)	0.0080 (10)	0.0030 (11)
O2	0.0639 (14)	0.0322 (11)	0.0909 (19)	−0.0061 (10)	0.0152 (13)	−0.0050 (11)
N1	0.0349 (11)	0.0403 (12)	0.0438 (13)	0.0003 (9)	0.0039 (9)	−0.0007 (10)
N2	0.0386 (11)	0.0293 (10)	0.0410 (12)	0.0025 (9)	0.0029 (9)	−0.0028 (9)
N3	0.0409 (12)	0.0361 (11)	0.0433 (12)	0.0066 (9)	−0.0015 (9)	−0.0036 (10)
C1	0.0403 (14)	0.0433 (15)	0.0411 (14)	−0.0040 (12)	−0.0014 (11)	0.0012 (12)
C2	0.0422 (14)	0.0343 (14)	0.0491 (16)	−0.0040 (11)	0.0006 (11)	−0.0014 (11)
C3	0.0363 (12)	0.0305 (12)	0.0306 (12)	0.0012 (10)	−0.0014 (9)	0.0015 (10)
C4	0.0371 (13)	0.0359 (13)	0.0380 (13)	0.0023 (11)	0.0020 (10)	−0.0004 (11)

C5	0.0449 (14)	0.0310 (13)	0.0357 (13)	−0.0036 (11)	−0.0029 (10)	0.0014 (10)
C6	0.0495 (15)	0.0290 (13)	0.0443 (15)	0.0032 (11)	−0.0052 (12)	−0.0022 (11)
C7	0.0356 (12)	0.0340 (13)	0.0341 (13)	0.0013 (10)	−0.0020 (9)	−0.0020 (10)
C8	0.0473 (15)	0.0339 (13)	0.0460 (15)	0.0052 (11)	0.0071 (12)	−0.0077 (11)
C9	0.0450 (16)	0.0376 (14)	0.0491 (16)	0.0085 (11)	0.0107 (12)	0.0009 (12)
C10	0.0498 (18)	0.0539 (18)	0.0571 (19)	0.0096 (14)	0.0045 (14)	−0.0032 (15)
C11	0.0410 (15)	0.0528 (18)	0.0590 (19)	0.0034 (12)	0.0115 (13)	−0.0033 (14)
C12	0.0348 (14)	0.0452 (16)	0.078 (2)	−0.0002 (12)	0.0109 (15)	0.0023 (15)
C13	0.0465 (19)	0.074 (3)	0.094 (3)	0.0025 (18)	−0.004 (2)	0.012 (2)

Geometric parameters (Å, º)

Br1—C5	1.894 (3)	C4—H4	0.9300
O1—C1	1.217 (4)	C4—C5	1.384 (4)
O2—C2	1.214 (4)	C5—C6	1.381 (4)
N1—C1	1.363 (4)	C6—H6	0.9300
N1—C7	1.402 (4)	C8—H8A	0.9700
N1—C11	1.472 (4)	C8—H8B	0.9700
N2—C2	1.365 (4)	C8—C9	1.457 (5)
N2—C3	1.397 (3)	C9—C10	1.176 (5)
N2—C8	1.477 (3)	C10—H10	0.9300
N3—C6	1.331 (4)	C11—H11A	0.9700
N3—C7	1.322 (4)	C11—H11B	0.9700
C1—C2	1.524 (4)	C11—C12	1.472 (5)
C3—C4	1.379 (4)	C12—C13	1.172 (6)
C3—C7	1.405 (4)	C13—H13	0.9300
C1—N1—C7	122.8 (2)	N3—C6—C5	120.9 (2)
C1—N1—C11	118.2 (2)	N3—C6—H6	119.5
C7—N1—C11	118.9 (2)	C5—C6—H6	119.5
C2—N2—C3	122.5 (2)	N1—C7—C3	119.3 (2)
C2—N2—C8	117.4 (2)	N3—C7—N1	116.8 (2)
C3—N2—C8	119.8 (2)	N3—C7—C3	123.9 (3)
C7—N3—C6	118.7 (2)	N2—C8—H8A	108.8
O1—C1—N1	123.3 (3)	N2—C8—H8B	108.8
O1—C1—C2	119.2 (3)	H8A—C8—H8B	107.7
N1—C1—C2	117.5 (2)	C9—C8—N2	114.0 (2)
O2—C2—N2	123.2 (3)	C9—C8—H8A	108.8
O2—C2—C1	119.0 (3)	C9—C8—H8B	108.8
N2—C2—C1	117.7 (2)	C10—C9—C8	175.8 (3)
N2—C3—C7	119.9 (2)	C9—C10—H10	180.0
C4—C3—N2	122.9 (2)	N1—C11—H11A	109.6
C4—C3—C7	117.3 (2)	N1—C11—H11B	109.6
C3—C4—H4	121.0	H11A—C11—H11B	108.1
C3—C4—C5	118.1 (2)	C12—C11—N1	110.1 (3)
C5—C4—H4	121.0	C12—C11—H11A	109.6
C4—C5—Br1	120.1 (2)	C12—C11—H11B	109.6
C6—C5—Br1	118.9 (2)	C13—C12—C11	178.3 (4)

C6—C5—C4	121.0 (3)	C12—C13—H13	180.0

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···O2^{i}	0.93	2.58	3.326 (4)	137

Symmetry code: (i) −*x*+1, *y*−1/2, −*z*+1/2.