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5-Bromo-*N*³-phenylpyrazine-2,3-diamine

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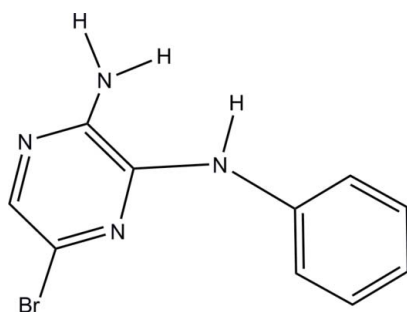
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.025; wR factor = 0.059; data-to-parameter ratio = 13.4.

In the title compound, $\text{C}_{10}\text{H}_9\text{BrN}_4$, the dihedral angle between the benzene and pyrazine rings is $61.34(5)^\circ$. Intermolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds and $\text{N}-\text{H}\cdots\pi$ interactions assemble the molecules into a three-dimensional network structure.

Related literature

For Cu or Pd catalysed C–N cross-coupling reactions, see: Fors *et al.* (2009); Liu *et al.* (2007).



Experimental

Crystal data

 $\text{C}_{10}\text{H}_9\text{BrN}_4$ $M_r = 265.12$

Monoclinic, $P2_1/c$
 $a = 7.4834(8)$ Å
 $b = 15.4038(17)$ Å
 $c = 9.2079(10)$ Å
 $\beta = 91.307(2)^\circ$
 $V = 1061.1(2)$ Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 3.85$ mm⁻¹
 $T = 293$ K
 $0.15 \times 0.12 \times 0.10$ mm

Data collection

Bruker SMART APEX
 diffractometer
 Absorption correction: multi-scan
 (SADABS; Bruker, 2005)
 $T_{\min} = 0.596$, $T_{\max} = 0.700$

5494 measured reflections
 1871 independent reflections
 1555 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.059$
 $S = 1.00$
 1871 reflections

140 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.33$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.33$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1B}\cdots\text{Cg1}^i$	0.86	2.63	3.436 (3)	157
$\text{N1}-\text{H1A}\cdots\text{N2}^{ii}$	0.86	2.22	3.084 (3)	169

Symmetry codes: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x, -y + 1, -z + 1$. Cg1 is the centroid of the C5–C10 ring.

Data collection: SMART (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); 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: SHELXL97.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2218).

References

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 Fors, B. P., Davis, N. R. & Buchwald, S. L. (2009). *J. Am. Chem. Soc.* **131**, 5766–5768.
 Liu, Y. F., Bai, Y. J., Zhang, J., Li, Y. Y., Jiao, J. P. & Qi, X. L. (2007). *Eur. J. Org. Chem.*, 6084–6088.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supporting information

Acta Cryst. (2009). E65, o1968 [doi:10.1107/S1600536809028554]

5-Bromo-*N*³-phenylpyrazine-2,3-diamine**Xiaohui Zhu****S1. Comment**

Cu or Pd catalyzed C—N cross-coupling reactions were studied recently (Liu *et al.*, 2007; Fors *et al.*, 2009), which reported that catalysts using certain ligands allow for the C—N cross-coupling reactions. Different to them, we got a cross-coupling product with high selectivity under microwave without catalyst.

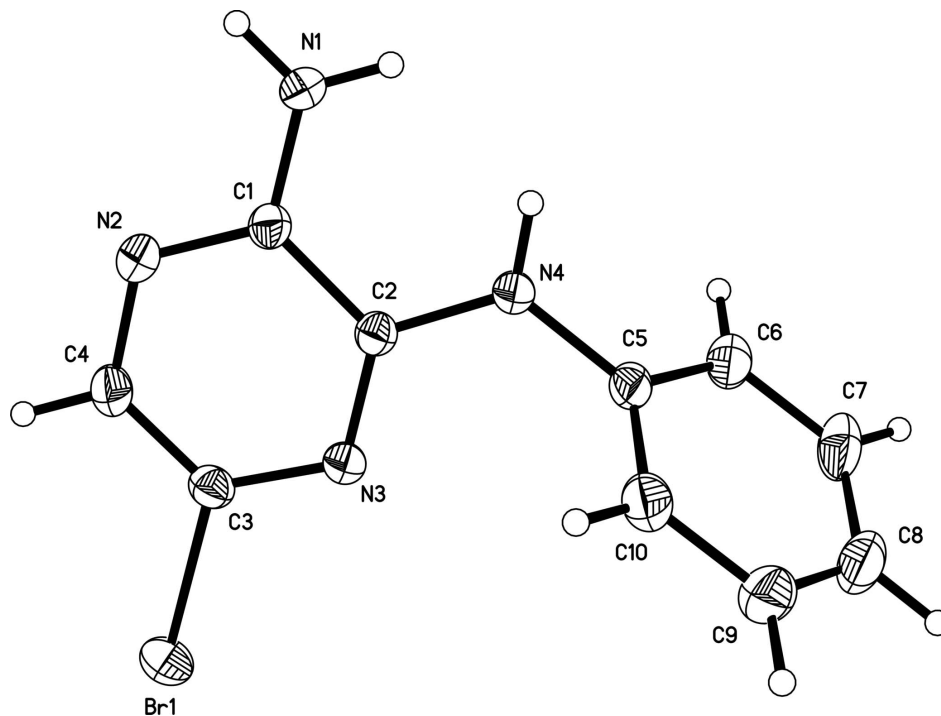
Here we report the crystal structure of the title compound. In (I) (Fig.1), the bond length to the bridging NH group are 1.377 (3) and 1.420 (3) Å. Moreover, intermolecular typical N—H···N (N···N 3.084 (3) Å) hydrogen bonds and N—H··· π [H··· π 2.633 (2) Å] interaction assemble molecules into a two-dimensional network structure.

S2. Experimental

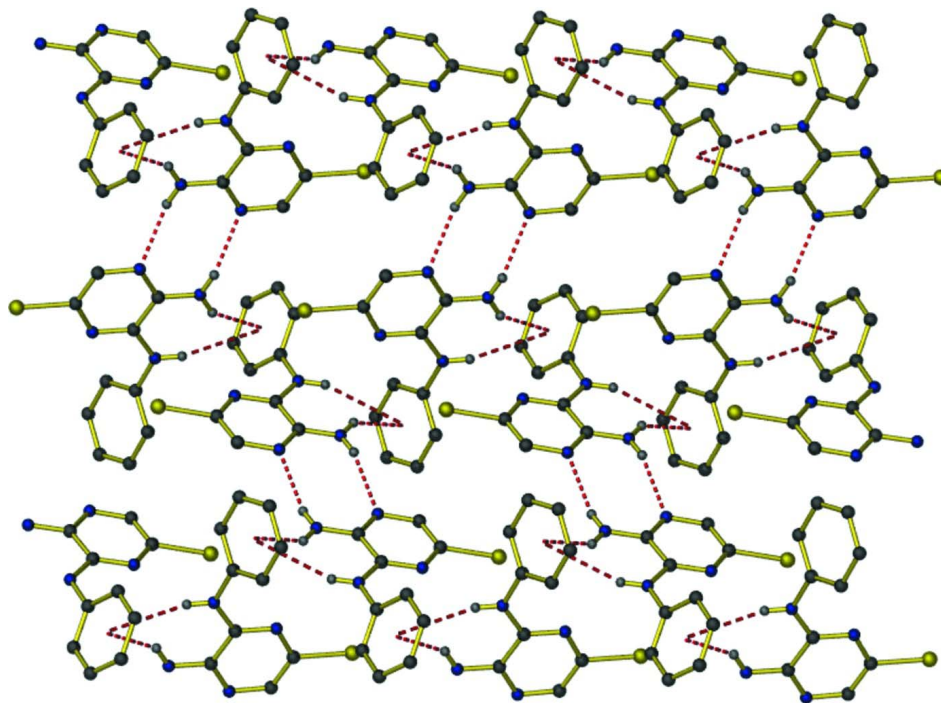
5-Bromo-2-aminopyrazine (10 mmol) and aniline (40 mmol) were added to a reaction kettle, then reacted 2 h at 413 K under microwave operation. The product was purified on a SiO₂ flash column to give a title product (yield 31%). Crystals of the title compound suitable for X-ray analysis were grown from a dichloromethane solution.

S3. Refinement

The C—H and N—H hydrogen atoms were placed in calculated positions, with distances C—H = 0.93 Å, N—H = 0.87 Å, and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C}, \text{N})$. Initially positions of the amino H atoms were refined but in the final cycles the N—H distances were constrained to 0.87 Å and all H atoms were treated as riding with $U_{\text{iso}}(\text{H})$ values of $1.5U_{\text{eq}}(\text{C}, \text{N})$.

**Figure 1**

The molecular structure of the title compound, showing 30% probability displacement ellipsoids.

**Figure 2**

The two-dimensional network structure formed by N—H...N hydrogen bonds and N—H... π interactions.

5-Bromo-*N*³-phenylpyrazine-2,3-diamine

Crystal data

C₁₀H₉BrN₄ $M_r = 265.12$ Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

 $a = 7.4834 (8) \text{ \AA}$ $b = 15.4038 (17) \text{ \AA}$ $c = 9.2079 (10) \text{ \AA}$ $\beta = 91.307 (2)^\circ$ $V = 1061.1 (2) \text{ \AA}^3$ $Z = 4$ $F(000) = 528$ $D_x = 1.660 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2474 reflections

 $\theta = 2.6\text{--}27.6^\circ$ $\mu = 3.85 \text{ mm}^{-1}$ $T = 293 \text{ K}$

Block, colorless

 $0.15 \times 0.12 \times 0.10 \text{ mm}$

Data collection

Bruker SMART APEX

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2005)

 $T_{\min} = 0.596$, $T_{\max} = 0.700$

5494 measured reflections

1871 independent reflections

1555 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.022$ $\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 2.6^\circ$ $h = -8 \rightarrow 8$ $k = -17 \rightarrow 18$ $l = -10 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.025$ $wR(F^2) = 0.059$ $S = 1.00$

1871 reflections

140 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: inferred from

neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.025P)^2 + 0.6504P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.002$ $\Delta\rho_{\max} = 0.33 \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -0.33 \text{ e \AA}^{-3}$

Extinction correction: SHELXL97 (Sheldrick,

2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0241 (11)

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	-0.05901 (4)	0.351301 (18)	1.09071 (3)	0.05020 (14)
N1	0.1466 (3)	0.39455 (14)	0.4791 (2)	0.0455 (5)
H1A	0.1000	0.4388	0.4334	0.046 (8)*

H1B	0.2400	0.3676	0.4472	0.075 (11)*
N2	-0.0254 (3)	0.43567 (13)	0.6710 (2)	0.0404 (5)
N3	0.1484 (2)	0.31467 (12)	0.84959 (19)	0.0319 (4)
N4	0.3193 (3)	0.27272 (13)	0.6497 (2)	0.0420 (5)
H4	0.2980	0.2595	0.5591	0.063 (9)*
C1	0.1017 (3)	0.38587 (14)	0.6195 (2)	0.0317 (5)
C2	0.1899 (3)	0.32331 (14)	0.7117 (2)	0.0302 (5)
C3	0.0152 (3)	0.36556 (15)	0.8955 (2)	0.0343 (5)
C4	-0.0699 (3)	0.42447 (16)	0.8104 (3)	0.0423 (6)
H4A	-0.1608	0.4579	0.8488	0.051*
C5	0.4259 (3)	0.21097 (15)	0.7267 (2)	0.0365 (6)
C6	0.4269 (4)	0.12553 (16)	0.6809 (3)	0.0446 (6)
H6	0.3565	0.1084	0.6014	0.054*
C7	0.5329 (4)	0.06590 (19)	0.7538 (3)	0.0564 (8)
H7	0.5338	0.0084	0.7229	0.068*
C8	0.6367 (4)	0.0902 (2)	0.8710 (3)	0.0613 (8)
H8	0.7056	0.0491	0.9209	0.074*
C9	0.6390 (4)	0.1748 (2)	0.9145 (3)	0.0589 (8)
H9	0.7108	0.1916	0.9934	0.071*
C10	0.5348 (3)	0.23602 (18)	0.8419 (3)	0.0468 (6)
H10	0.5383	0.2938	0.8709	0.056*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0541 (2)	0.0615 (2)	0.03565 (17)	0.00683 (14)	0.01461 (11)	0.00123 (12)
N1	0.0648 (15)	0.0406 (12)	0.0314 (11)	0.0182 (11)	0.0047 (10)	0.0082 (9)
N2	0.0466 (13)	0.0353 (11)	0.0392 (12)	0.0102 (9)	0.0014 (9)	0.0047 (9)
N3	0.0345 (11)	0.0327 (10)	0.0288 (10)	0.0035 (8)	0.0036 (8)	0.0018 (8)
N4	0.0504 (13)	0.0451 (12)	0.0310 (11)	0.0194 (10)	0.0094 (9)	0.0070 (9)
C1	0.0369 (13)	0.0262 (11)	0.0320 (12)	0.0014 (10)	-0.0003 (10)	-0.0008 (9)
C2	0.0330 (13)	0.0265 (11)	0.0312 (12)	0.0008 (9)	0.0013 (10)	0.0001 (9)
C3	0.0375 (13)	0.0359 (13)	0.0297 (12)	-0.0004 (10)	0.0048 (10)	-0.0004 (10)
C4	0.0433 (15)	0.0400 (14)	0.0440 (15)	0.0124 (11)	0.0085 (11)	0.0005 (11)
C5	0.0339 (13)	0.0404 (14)	0.0356 (12)	0.0084 (10)	0.0107 (10)	0.0087 (11)
C6	0.0408 (15)	0.0416 (15)	0.0516 (16)	0.0068 (11)	0.0040 (12)	0.0028 (12)
C7	0.0502 (17)	0.0404 (15)	0.079 (2)	0.0149 (13)	0.0099 (15)	0.0084 (14)
C8	0.0492 (18)	0.069 (2)	0.066 (2)	0.0229 (15)	0.0049 (15)	0.0211 (16)
C9	0.0419 (16)	0.084 (2)	0.0504 (17)	0.0121 (15)	-0.0041 (13)	0.0015 (15)
C10	0.0438 (15)	0.0478 (15)	0.0489 (15)	0.0067 (12)	0.0064 (12)	-0.0016 (13)

Geometric parameters (Å, °)

Br1—C3	1.906 (2)	C4—H4A	0.9300
N1—C1	1.349 (3)	C5—C10	1.378 (4)
N1—H1A	0.8699	C5—C6	1.382 (3)
N1—H1B	0.8700	C6—C7	1.378 (4)
N2—C1	1.319 (3)	C6—H6	0.9300

N2—C4	1.344 (3)	C7—C8	1.368 (4)
N3—C2	1.320 (3)	C7—H7	0.9300
N3—C3	1.344 (3)	C8—C9	1.364 (4)
N4—C2	1.377 (3)	C8—H8	0.9300
N4—C5	1.420 (3)	C9—C10	1.385 (4)
N4—H4	0.8700	C9—H9	0.9300
C1—C2	1.436 (3)	C10—H10	0.9300
C3—C4	1.349 (3)		
C1—N1—H1A	115.8	C3—C4—H4A	119.4
C1—N1—H1B	119.8	C10—C5—C6	119.6 (2)
H1A—N1—H1B	121.8	C10—C5—N4	120.8 (2)
C1—N2—C4	117.7 (2)	C6—C5—N4	119.5 (2)
C2—N3—C3	115.85 (19)	C7—C6—C5	119.5 (3)
C2—N4—C5	124.36 (19)	C7—C6—H6	120.2
C2—N4—H4	114.5	C5—C6—H6	120.2
C5—N4—H4	114.3	C8—C7—C6	120.8 (3)
N2—C1—N1	119.0 (2)	C8—C7—H7	119.6
N2—C1—C2	120.2 (2)	C6—C7—H7	119.6
N1—C1—C2	120.8 (2)	C9—C8—C7	119.7 (3)
N3—C2—N4	121.6 (2)	C9—C8—H8	120.1
N3—C2—C1	121.5 (2)	C7—C8—H8	120.1
N4—C2—C1	116.92 (19)	C8—C9—C10	120.4 (3)
N3—C3—C4	123.6 (2)	C8—C9—H9	119.8
N3—C3—Br1	117.62 (16)	C10—C9—H9	119.8
C4—C3—Br1	118.81 (18)	C5—C10—C9	119.8 (3)
N2—C4—C3	121.2 (2)	C5—C10—H10	120.1
N2—C4—H4A	119.4	C9—C10—H10	120.1
C4—N2—C1—N1	178.7 (2)	N3—C3—C4—N2	0.3 (4)
C4—N2—C1—C2	-1.1 (3)	Br1—C3—C4—N2	-178.49 (19)
C3—N3—C2—N4	-177.5 (2)	C2—N4—C5—C10	-59.7 (3)
C3—N3—C2—C1	2.3 (3)	C2—N4—C5—C6	123.5 (3)
C5—N4—C2—N3	-3.5 (4)	C10—C5—C6—C7	1.9 (4)
C5—N4—C2—C1	176.6 (2)	N4—C5—C6—C7	178.8 (2)
N2—C1—C2—N3	-0.9 (3)	C5—C6—C7—C8	0.1 (4)
N1—C1—C2—N3	179.4 (2)	C6—C7—C8—C9	-1.6 (5)
N2—C1—C2—N4	179.0 (2)	C7—C8—C9—C10	0.9 (5)
N1—C1—C2—N4	-0.8 (3)	C6—C5—C10—C9	-2.6 (4)
C2—N3—C3—C4	-2.1 (3)	N4—C5—C10—C9	-179.4 (2)
C2—N3—C3—Br1	176.66 (16)	C8—C9—C10—C5	1.2 (4)
C1—N2—C4—C3	1.3 (4)		

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—H1B...Cg1 ⁱ	0.86	2.63	3.436 (3)	157

N1—H1A \cdots N2 ⁱⁱ	0.86	2.22	3.084 (3)	169
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Symmetry codes: (i) $x, -y+1/2, z-1/2$; (ii) $-x, -y+1, -z+1$.