Crystal structures of $N$-(pyridin-2-ylmethyl)-pyrazine-2-carboxamide (monoclinic polymorph) and $N$-(pyridin-4-ylmethyl)pyrazine-2-carboxamide

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The title compounds, $C_{11}H_{10}N_4O$ (HL1) and $C_{11}H_{10}N_4O$ (HL2), are pyridine 2-ylmethyl and 4-ylmethyl derivatives, respectively, of pyrazine-2-carboxamide. HL1 was measured at 153 K and crystallized in the monoclinic space group $P2_1/c$ with $Z = 4$. There has been a report of the same structure measured at room temperature but assumed to crystallize in the triclinic space group $P\bar{1}$ with $Z = 4$ [Sasan et al. (2008). Monatsh. Chem. 139, 773–780]. In HL1, the pyridine ring is inclined to the pyrazine ring by $61.34 (6)^\circ$, while in HL2 this dihedral angle is $84.33 (12)^\circ$. In both molecules, there is a short $N-H\cdots N$ interaction involving the pyrazine carboxamide unit. In the crystal of HL1, molecules are linked by $N-H\cdots N$ hydrogen bonds, forming inversion dimers with an $R_2^2(10)$ ring motif. The dimers are linked *via* bifurcated-acceptor $C-H\cdots O$ hydrogen bonds, forming sheets lying parallel to (102). The sheets are linked *via* $C-H\cdots N$ hydrogen bonds, forming a three-dimensional structure. In the crystal of HL2, molecules are linked by $N-H\cdots N$ and $C-H\cdots N$ hydrogen bonds to form chains propagating along [010]. The chains are linked *via* $C-H\cdots O$ hydrogen bonds, forming sheets lying parallel to (100). Within the sheets there are $\pi-\pi$ interactions involving neighbouring pyrazine rings [inter-centroid distance = 3.711 (15) Å]. Adjacent sheets are linked *via* parallel slipped $\pi-\pi$ interactions involving inversion-related pyridine rings [inter-centroid distance = 3.6395 (17) Å], forming a three-dimensional structure.

1. Chemical context

The title compounds form part of a series of ligands synthesized in order to study their coordination chemistry with $3d$ transition metals (Cati, 2002). They have been used to construct coordination polymers and multi-nuclear compounds, and to study their magnetic properties.
properties (Cati et al., 2004). Similar ligands have been synthesized by other groups who have studied, for example, the magnetic properties of some copper(II) complexes (Hausmann et al., 2003; Kingele et al., 2007).

2. Structural commentary

The molecular structure of ligand HL1 is illustrated in Fig. 1. HL1 was measured at 153 K and crystallized in the monoclinic space group $P_{2_1}/c$ with $Z = 4$. The $\beta$ angle is 91.461 (11)$^\circ$ and the systematic absences, the $R_{int}$ value (0.0348) and the successful refinement $[R_1 (I > 2\sigma(I)) = 0.0319]$ clearly show that at 153 K the space group is monoclinic $P_{2_1}/c$. The same structure measured at room temperature was reported to crystallize in the triclinic space group $P\overline{1}$. However, the three cell angles are close 90 (2)$^\circ$ [$\alpha = 91.802 (6)$, $\beta = 89.834 (7)$, $\gamma = 91.845 (6)$$^\circ$] and the crystal used was a very narrow needle. The final $R_1 (I > 2\sigma(I))$ factor was rather high at 0.0699, hence it is possible that the choice of crystal system and space group are incorrect. However, this could not be confirmed when analysing the coordinates using the AddSymm routine in PLATON (Spek, 2009).

In the molecule of HL1 there is a short N⋯H⋯N hydrogen bond present in the pyrazine carboxamide unit (Table 1), and the amide group, C5(≡O1)N3, is approximately coplanar with the pyrazine (N1/N2/C1–C4) ring [dihedral angle = 2.56 (14)$^\circ$]. The pyrazine and pyridine (N4/C7–C10) rings are inclined to one another by 61.34 (6)$^\circ$. The triclinic structure mentioned above, the same angle in the two independent molecules is 63.31 (13) and 61.94 (13)$^\circ$.

The molecular structure of HL2 is illustrated in Fig. 2. Here too there is a short intramolecular N⋯H⋯N contact involving the pyrazine carboxamide unit (Table 2), and the amide group, C5(≡O1)N3, is almost coplanar with the pyrazine (N1/N2/C1–C4) ring with a dihedral angle of 3.9 (3)$^\circ$. Here the pyrazine and pyridine (N4/C7–C10) rings are almost normal to one another with a dihedral angle of 84.33 (12)$^\circ$.

| Table 1 | Hydrogen-bond geometry (Å, $^\circ$) for HL1. |
|---------|------------------------------------------------|
| $D$⋯$H$⋯$A$ | $D$⋯$A$ | $H$⋯$D$ | $D$⋯$A$ | $D$⋯$H$⋯$A$ |
| N3⋯H3=N⋯N1 | 0.90 (16) | 2.33 (15) | 2.71 (15) | 105.4 (11) |
| N3⋯H3=N⋯N4$'$ | 0.90 (16) | 2.20 (16) | 2.99 (14) | 145.6 (13) |
| C3⋯H3⋯O1$^a$ | 0.95 | 2.51 | 3.15 (15) | 125 |
| C4⋯H4⋯O1$^a$ | 0.95 | 2.56 | 3.17 (15) | 123 |
| C10⋯H10⋯N2$^a$ | 0.95 | 2.62 | 3.57 (17) | 174 |

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

| Table 2 | Hydrogen-bond geometry (Å, $^\circ$) for HL2. |
|---------|------------------------------------------------|
| $D$⋯$H$⋯$A$ | $D$⋯$A$ | $H$⋯$D$ | $D$⋯$A$ | $D$⋯$H$⋯$A$ |
| N3⋯H3=N⋯N1 | 0.83 (3) | 2.27 (3) | 2.71 (3) | 114 (2) |
| N3⋯H3=N⋯N2$'$ | 0.83 (3) | 2.52 (3) | 3.21 (3) | 142 (2) |
| C2⋯H2⋯N1$^a$ | 0.93 | 2.47 | 3.31 (3) | 151 |
| C8⋯H8⋯O1$^a$ | 0.93 | 2.55 | 3.37 (3) | 148 |

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

In the crystal of HL1, molecules are linked by N—H···N hydrogen bonds, forming inversion dimers with an $R_2^2(10)$ ring motif. The dimers are linked via bifurcated-acceptor C—H···O hydrogen bonds, forming sheets lying parallel to (102) (see Table 1 and Fig. 3). The sheets are linked via C—H···N hydrogen bonds, forming a three-dimensional structure (Table 1 and Fig. 4).

In the crystal of HL2, molecules are linked by N—H···N and C—H···N hydrogen bonds to form chains propagating along [010], as shown in Table 2 and Fig. 5. The chains are linked via C—H···O hydrogen bonds, forming sheets lying parallel to (100). Within the sheets there are $\pi$–$\pi$ interactions involving neighbouring pyrazine rings [$Cg1\cdots Cg1^i = 3.7113 (15)$ Å; $Cg1$ is the centroid of the pyrazine ring N1/N2/C1–C4; symmetry code: (i) = $x$, $-y + \frac{1}{2}$, $z - \frac{1}{2}$]. The sheets are linked via slipped parallel $\pi$–$\pi$ interactions involving inversion-related pyridine rings [$Cg2\cdots Cg2^{ii} = 3.6395 (11)$ Å, normal distance = 3.4164 (11), slippage = 1.255 Å; $Cg2$ is the centroid of pyridine ring N4/C7–C11; symmetry code: (ii) = $-x$, $-y$, $-z$], forming a three-dimensional structure (Table 2 and Fig. 6).

4. Database survey

A search of the Cambridge Structural Database (Version 5.35, last update November 2013; Allen, 2002) indicated the presence of 282 structures containing the pyrazine-2-carboxamide unit. 81 of these concern pyrazine-2-carboxamide itself. There were 10 hits for complexes of ligand HL1. These include a cobalt(III) (Hellyer et al., 2009), a chromium(III) (Khavasi et al., 2010) and four copper(II) complexes (Mohamadou et al., 2012; Khavasi et al., 2011), all of which are mononuclear with the ligand coordinating in a tridentate manner. There are also two polymeric mercury chloride complexes (Khavasi & Sadegh, 2010), a binuclear manganese chloride complex (Khavasi et al., 2009), and a polymeric silver tetrafluoroborate complex (Hellyer et al., 2009), where the ligand coordinates in a bis-monodentate manner. Plus the report of the ligand itself as mentioned above (Sasan et al., 2008). For ligand HL2 there were no hits.
5. Synthesis and crystallization

The precursor pyrazine-2-carboxylic acid methyl ester (2-pze) was prepared following the procedure described by Alvarez-Ibarra et al. (1994). 6.21 g (50 mmol) of pyrazine-2-carboxylic acid were added to 50 ml of absolute methanol in a two-necked flask (100 ml). The mixture was heated to 303 K and then 0.4 ml of concentrated sulfuric acid was added slowly. The mixture was heated for 23 h, at least. It was then poured over ice and made alkaline using NaOH (2 M). A yellow band of 2-(aminomethyl)pyridine remained on the column. After evaporation, the ligand could be recrystallized from diethyl ether, acetonitrile or ethyl acetate. H

L1 was prepared by refluxing 2-pze (1.73 g, 16 mmol) in 12 ml of methanol, for 6 h in a two-necked flask (50 ml). H

2 was prepared using the same procedure as for H

L1. 2-pze (1.38 g, 10 mmol) with, this time, an excess of 4-(aminomethyl)pyridine (1.73 g, 16 mmol) were refluxed in 20 ml of methanol, for 20 h in a two-necked flask (50 ml). 4-(aminomethyl)pyridine (1g, 10 mmol) was then added to the red solution. After 4 h the solution was evaporated to about 8 ml. H

L2 crystallized out at room temperature. About 20 ml of diethyl ether was added to filtrate the product. It was then recrystallized from a mixture of 3 ml of methanol and 40 ml of diethyl ether to give colourless blocks (yield 84%; m.p. 422 K).

Analysis for C\textsubscript{11}H\textsubscript{10}N\textsubscript{4}O (M \textsubscript{r} = 214.46 g/mol) Calculated (%) C: 61.67 H: 4.71 N: 26.15; Found (%) C: 61.80 H: 4.76 N: 26.45. Spectroscopic data are available in the supporting information.

HL2 was prepared using the same procedure as for HL1. 2-pze (1.38 g, 10 mmol) with, this time, an excess of 4-(aminomethyl)pyridine (1.73 g, 16 mmol) were refluxed in 20 ml of methanol, for 20 h in a two-necked flask (50 ml). 4-(aminomethyl)pyridine (1g, 10 mmol) was then added to the red solution. After 4 h the solution was evaporated to about 8 ml. H

L2 crystallized out at room temperature. About 20 ml of diethyl ether was added to filtrate the product. It was then recrystallized from a mixture of 3 ml of methanol and 40 ml of diethyl ether to give colourless blocks (yield 84%; m.p. 422 K).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The NH H atoms were located in difference Fourier maps and freely refined. The C-bound H atoms were included in calculated positions and treated as riding atoms: C—H = 0.95 Å for HL1 and = 0.93 Å for HL2, with U\textsubscript{eq}(H) = 1.2U\textsubscript{eq}(C).

Acknowledgements

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Table 3

| Crystal data | HL1 | HL2 |
|--------------|-----|-----|
| Chemical formula | C\textsubscript{11}H\textsubscript{10}N\textsubscript{4}O | C\textsubscript{11}H\textsubscript{10}N\textsubscript{4}O |
| M\textsubscript{r} | 214.23 | 214.23 |
| Crystal system, space group | Monoclinic, P2\textsubscript{1}/c | Monoclinic, P2\textsubscript{1}/c |
| Temperature (K) | 153 | 293 |
| a, b, c (Å) | 4.1527 (4), 20.4629 (18), 12.0106 (11) | 13.8564 (14), 11.1841 (11), 6.9122 (10) |
| β (°) | 91.461 (11) | 104.356 (14) |
| V (Å\textsuperscript{3}) | 1020.28 (16) | 1037.7 (2) |
| Z | 4 | 4 |
| Radiation type | Mo Kα | Mo Kα |
| μ (mm\textsuperscript{-1}) | 0.30 | 0.09 |
| Crystal size (mm) | 0.50 × 0.40 × 0.35 | 0.38 × 0.30 × 0.19 |

Data collection

| Diffractometer | Stoe IPDS 1 | Stoe AED2 four-circle |
|----------------|-------------|----------------------|
| No. of measured, independent and observed | 7822, 1958, 1548 | 4132, 1937, 1198 |
| [I > 2σ(I)] reflections | 0.035 | 0.032 |
| sin(θ)/λ max (Å\textsuperscript{-1}) | 0.615 | 0.605 |

Refinement

| R(F\textsuperscript{2}) > 2σ(F\textsuperscript{2}), wR(F\textsuperscript{2}), S | 0.032, 0.088, 1.03 | 0.054, 0.127, 1.10 |
|-----------------|----------------|-----------------|
| No. of reflections | 1958 | 1937 |
| No. of parameters | 149 | 150 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement | H atoms treated by a mixture of independent and constrained refinement |

Δρ\textsubscript{max}, Δρ\textsubscript{min} (e Å\textsuperscript{-3}) | 0.17, –0.17 | 0.17, –0.16 |

Crystallization details:

- HL1: Prepared following the procedure described by Alvarez-Ibarra et al. (1994).
- HL2: Prepared using the same procedure as for HL1.

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supporting information

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Crystal structures of N-(pyridin-2-ylmethyl)pyrazine-2-carboxamide (monoclinic polymorph) and N-(pyridin-4-ylmethyl)pyrazine-2-carboxamide

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Computing details
Data collection: EXPOSE in IPDSI (Stoe & Cie, 1997) for HL1; STADI4 (Stoe & Cie, 1997) for HL2. Cell refinement: CELL in IPDSI (Stoe & Cie, 1997) for HL1; STADI4 (Stoe & Cie, 1997) for HL2. Data reduction: INTEGRATE in IPDSI (Stoe & Cie, 1997) for HL1; X-RED (Stoe & Cie, 1997) for HL2. For both compounds, program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2013 (Sheldrick, 2008); molecular graphics: Mercury (Macrae et al., 2008); software used to prepare material for publication: SHELXL2013 (Sheldrick, 2008), PLATON (Spek, 2009) and publCIF (Westrip, 2010).

(HL1) N-(Pyridin-2-ylmethyl)pyrazine-2-carboxamide

Crystal data

| Parameter | Value |
|-----------|-------|
| C₁₁H₁₀N₄O |       |
| Mr        | 214.23 |
| Monoclinic, P2₁/c |       |
| a         | 4.1527 (4) Å |
| b         | 20.4629 (18) Å |
| c         | 12.0106 (11) Å |
| β         | 91.461 (11)° |
| V         | 1020.28 (16) Å³ |
| Z         | 4     |

F(000) = 448
Dₐ = 1.395 Mg m⁻³
Mo Kα radiation, λ = 0.71073 Å
Cell parameters from 6532 reflections
θ = 2.0–25.9°
μ = 0.10 mm⁻¹
T = 153 K
Block, colourless
0.50 × 0.40 × 0.35 mm

Data collection

| Parameter | Value |
|-----------|-------|
| Stoe IPDS 1 diffractometer |       |
| Radiation source: fine-focus sealed tube |       |
| Plane graphite monochromator |       |
| φ rotation scans |       |
| 7822 measured reflections |       |
| 1548 reflections with I > 2σ(I) |       |
| Rint = 0.035 |       |
| θmax = 25.9°, θmin = 2.0° |       |
| h = −5→5 |       |
| k = −25→25 |       |
| l = −14→14 |       |

Refinement

| Parameter | Value |
|-----------|-------|
| Refinement on F² |       |
| Least-squares matrix: full |       |
| R(F² > 2σ(F²)) = 0.032 |       |
| wR(F²) = 0.088 |       |
| S = 1.03 |       |
| 1958 reflections |       |
| 149 parameters |       |
| 0 restraints |       |

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

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$w = 1/\sigma^2(F_o^2) + (0.0539P)^2 + 0.0704P$

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

$\Delta \rho_{\text{max}} = 0.17 \text{ e Å}^{-3}$
$\Delta \rho_{\text{min}} = -0.17 \text{ e Å}^{-3}$

$\Delta(\sigma)_{\text{max}} < 0.001$

Special details

Experimental. Spectroscopic data for HL1: $^1$H NMR (400 MHz, DMSO-d$_6$; code Hh/NH, Hl/C3, Hn/C1, Hm/C2, Hb/C11, Hd/C9, He/C8, Hc/C10, Hg/C6): 9.50 (t, 1H, Jhg = 6.0, Hh); 9.23 (d, 1H, Jlm = 1.5, Hl); 8.91 (d, 1H, Jnm = 2.5, Hn); 8.78 (dd, 1H, Jbc = 4.8, Jbd = 1.8, Hb); 8.63 (dd, 1H, Jcd = 7.7, Jdb = 1.8, Hd); 8.53 (ddd, 1H, Jbc = 4.8, Jbd = 1.8, Jbe = 0.8, Hc); 7.76 (td, 1H, Jdc = 7.7, Jdb = 1.8, Hed); 7.35 (d, 1H, Jed = 7.9, He); 6.64 (d, 2H, Jgh = 6.0, He). $^{13}$C NMR (400 MHz, DMSO-d$_6$): 163.9, 158.6, 149.7, 148.6, 145.5, 144.4, 144.3, 137.6, 123.1, 121.9, 45.0. IR (KBr pellet, cm$^{-1}$): 3248 (m), 3066 (w), 3018 (w), 2949 (w), 1669 (versus), 1593 (m), 1570 (m), 1517 (versus), 1478 (m), 1440 (s), 1423 (s), 1389 (s), 1350 (m), 1320 (m), 1287 (s), 1250 (m), 1221 (m), 1168 (s), 1148 (m), 1103 (m), 1055 (m), 1021 (s), 1000 (m), 975 (m), 870 (w), 840 (w), 776 (m), 753 (s), 707 (m), 634 (m), 611 (m), 528 (m), 444 (m).

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)

|    | x     | y     | z     | U$_{eq}$/$U_{eq}$ |
|----|-------|-------|-------|------------------|
| N1 | 0.7345 (3) | 0.30055 (5) | 0.42625 (8) | 0.0260 (2) |
| N2 | 0.7780 (3) | 0.16917 (5) | 0.49125 (9) | 0.0343 (3) |
| N3 | 0.4290 (2) | 0.38859 (5) | 0.55546 (8) | 0.0224 (2) |
| H3N| 0.514 (4)  | 0.3982 (7)  | 0.4892 (13) | 0.037 (4)*   |
| N4 | 0.5222 (3) | 0.53951 (5) | 0.66045 (8) | 0.0293 (3) |
| O1 | 0.3074 (2) | 0.30857 (4) | 0.67870 (7) | 0.0344 (2) |
| C1 | 0.6100 (3) | 0.27903 (5) | 0.52119 (9) | 0.0215 (3) |
| C2 | 0.6318 (3) | 0.21416 (6) | 0.55317 (10) | 0.0287 (3) |
| H2 | 0.5401 | 0.2011 | 0.6213 | 0.034* |
| C3 | 0.9010 (3) | 0.19099 (6) | 0.39702 (10) | 0.0305 (3) |
| H3 | 1.0071 | 0.1609 | 0.3501 | 0.037* |
| C4 | 0.8800 (3) | 0.25567 (6) | 0.36486 (10) | 0.0290 (3) |
| H4 | 0.9724 | 0.2686 | 0.2967 | 0.035* |
| C5 | 0.4355 (3) | 0.32697 (6) | 0.59277 (9) | 0.0229 (3) |
| C6 | 0.2435 (3) | 0.43932 (6) | 0.60984 (10) | 0.0263 (3) |
| H6A| 0.0627 | 0.4186 | 0.6488 | 0.032* |
| H6B| 0.1503 | 0.4688 | 0.5522 | 0.032* |
| C7 | 0.4391 (3) | 0.47934 (5) | 0.69249 (9) | 0.0219 (3) |
| C8 | 0.5266 (3) | 0.45428 (6) | 0.79615 (10) | 0.0271 (3) |
| H8 | 0.4640 | 0.4113 | 0.8163 | 0.033* |
| C9 | 0.7051 (3) | 0.49220 (6) | 0.86977 (10) | 0.0312 (3) |
| H9 | 0.7682 | 0.4757 | 0.9410 | 0.037* |
| C10| 0.7906 (4) | 0.55455 (6) | 0.83801 (11) | 0.0350 (3) |
| H10| 0.9115 | 0.5822 | 0.8870 | 0.042* |
| C11| 0.6957 (4) | 0.57556 (6) | 0.73353 (11) | 0.0376 (3) |
| H11| 0.7569 | 0.6183 | 0.7117 | 0.045* |

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### Atomic Displacement Parameters (Å²)

|       | $U^{11}$  | $U^{22}$  | $U^{33}$  | $U^{12}$  | $U^{13}$  | $U^{23}$  |
|-------|-----------|-----------|-----------|-----------|-----------|-----------|
| N1    | 0.0305 (6) | 0.0246 (5) | 0.0231 (5) | −0.0011 (4) | 0.0045 (4) | −0.0005 (4) |
| N2    | 0.0434 (7) | 0.0239 (5) | 0.0356 (6) | 0.0046 (5) | 0.0043 (5) | −0.0006 (4) |
| N3    | 0.0263 (5) | 0.0207 (5) | 0.0201 (5) | 0.0007 (4) | 0.0020 (4) | −0.0008 (4) |
| N4    | 0.0412 (7) | 0.0219 (5) | 0.0249 (5) | 0.0016 (4) | 0.0022 (4) | 0.0007 (4)  |
| O1    | 0.0454 (6) | 0.0295 (5) | 0.0288 (5) | 0.0000 (4) | 0.0154 (4) | 0.0036 (4)  |
| C1    | 0.0219 (6) | 0.0217 (6) | 0.0208 (5) | −0.0024 (5) | −0.0014 (4) | −0.0008 (4) |
| C2    | 0.0369 (8) | 0.0247 (6) | 0.0246 (6) | 0.0006 (5) | 0.0032 (5) | 0.0016 (5)  |
| C3    | 0.0327 (7) | 0.0275 (6) | 0.0313 (7) | 0.0029 (5) | 0.0039 (5) | −0.0067 (5) |
| C4    | 0.0321 (7) | 0.0305 (6) | 0.0246 (6) | −0.0012 (5) | 0.0056 (5) | −0.0028 (5) |
| C5    | 0.0233 (6) | 0.0242 (6) | 0.0211 (6) | −0.0021 (5) | −0.0003 (5) | −0.0001 (4) |
| C6    | 0.0244 (7) | 0.0248 (6) | 0.0296 (6) | 0.0062 (5) | −0.0010 (5) | −0.0021 (5) |
| C7    | 0.0210 (6) | 0.0213 (6) | 0.0235 (6) | 0.0055 (5) | 0.0057 (4) | −0.0011 (4) |
| C8    | 0.0275 (7) | 0.0258 (6) | 0.0281 (6) | 0.0005 (5) | 0.0024 (5) | 0.0046 (5)  |
| C9    | 0.0333 (7) | 0.0374 (7) | 0.0226 (8) | 0.0044 (6) | −0.0001 (5) | 0.0010 (5)  |
| C10   | 0.0420 (8) | 0.0310 (7) | 0.0317 (7) | −0.0002 (6) | −0.0034 (6) | −0.0093 (5) |
| C11   | 0.0554 (9) | 0.0207 (6) | 0.0366 (7) | −0.0046 (6) | −0.0022 (6) | −0.0006 (5) |

### Geometric Parameters (Å, °)

|       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|
| N1—C4 | 1.3323 (16) | C3—H3 | 0.9500 |
| N1—C1 | 1.3386 (15) | C4—H4 | 0.9500 |
| N2—C3 | 1.3307 (17) | C6—C7 | 1.5082 (16) |
| N2—C2 | 1.3387 (16) | C6—H6A | 0.9900 |
| N3—C5 | 1.3382 (15) | C6—H6B | 0.9900 |
| N3—C6 | 1.4570 (15) | C7—C8 | 1.3865 (17) |
| N3—H3N | 0.901 (16) | C8—C9 | 1.3784 (18) |
| N4—C7 | 1.3379 (15) | C8—H8 | 0.9500 |
| N4—C11 | 1.3422 (17) | C9—C10 | 1.3806 (18) |
| O1—C5 | 1.2319 (14) | C9—H9 | 0.9500 |
| C1—C2 | 1.3842 (16) | C10—C11 | 1.3745 (19) |
| C1—C5 | 1.5028 (16) | C10—H10 | 0.9500 |
| C2—H2 | 0.9500 | C11—H11 | 0.9500 |
| C3—C4 | 1.3808 (18) |     |     |     |     |     |

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Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N3—H3N···N1 | 0.901 (16) | 2.332 (15) | 2.7136 (15) | 105.4 (11) |
| N3—H3N···N4i | 0.901 (16) | 2.206 (16) | 2.9929 (15) | 145.6 (13) |
| C3—H3···O1ii | 0.95 | 2.51 | 3.1544 (15) | 125 |
| C4—H4···O1ii | 0.95 | 2.56 | 3.1748 (15) | 123 |
| C10—H10···N2iii | 0.95 | 2.62 | 3.5678 (17) | 174 |

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

(HL2) N-(Pyridin-4-ylmethyl)pyrazine-2-carboxamide

Crystal data

C_{11}H_{10}N_{4}O

\( M_r = 214.23 \)

Monoclinic, \( P2_1/c \)  
\( a = 13.8564 \) Å  
\( b = 11.1841 \) Å  
\( c = 6.9122 \) Å  
\( \beta = 104.356 \)°  
\( V = 1037.7 \) (2) Å³  
\( Z = 4 \)

\( F(000) = 448 \)  
\( D_a = 1.371 \) Mg m⁻³  
Mo Ka radiation, \( \lambda = 0.71073 \) Å  
Cell parameters from 20 reflections  
\( \theta = 10.4–17.6° \)  
\( \mu = 0.09 \) mm⁻¹  
\( T = 293 \) K  
Block, colourless  
0.38 × 0.30 × 0.19 mm
Data collection

Stoe AED2 four-circle diffractometer
Radiation source: fine-focus sealed tube
Plane graphite monochromator
2θ/ω scans
4132 measured reflections
1937 independent reflections
1198 reflections with I > 2σ(I)

Rint = 0.032
θmax = 25.5°, θmin = 2.4°

θ = −16→16
k = −13→0
l = −8→8

2 standard reflections every 60 min
Intensity decay: 2%

Refinement

Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.054
wR(F²) = 0.127
S = 1.10
1937 reflections
150 parameters
0 restraints
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(Fo²) + (0.0426P)² + 0.1904P]
where P = (Fo² + 2Fc²)/3

(Δρ)max = 0.17 e Å⁻³
(Δρ)min = −0.16 e Å⁻³

Extinction correction: SHELXL2013 (Sheldrick, 2008), Fc* = kFc[1 + 0.001xFc²λ³/sin(2θ)]⁻¹/₄
Extinction coefficient: 0.014 (2)

Special details

Experimental. Spectroscopic data for HL2: ¹H NMR (400 MHz, DMSO-d₆; code Hb/NH, HI/C3, Hn/C1, Hm/C2, Hb/C11, Hd/C9, Ha/C11/, He/C8, Hg/C6): 9.63 (t, 1H, Jhg = 6.3, Hh); 9.21 (d, 1H, Jlm = 1.5, Hl); 8.90 (d, 1H, Jnm = 2.5, Hn); 8.77 (dd, 1H, Jmn = 2.5, Jml = 1.5, Hm); 8.49 (dd, 2H, Jba = 4.4, Jbe = 1.6, Hb = Hd); 7.31 (dd, 2H, Jab = 4.4, Jad = 1.6, Hg = He); 4.54 (d, 2H, Jgh = 6.3, Hg). ¹³C NMR (400 MHz, DMSO-d₆): 164.2, 150.4, 149.0, 148.5, 145.4, 144.5, 144.3, 123.0, 42.4. IR (KBr pellet, cm⁻¹): 3366 (versus), 3089 (s), 3050 (m), 3031 (s), 2967 (m), 2935 (s), 1966 (w), 1924 (w), 1834 (w), 1674 (versus), 1634 (s), 1602 (versus), 1585 (s), 1564 (s) 1526 (versus), 1467 (versus), 1429 (versus), 1415 (versus), 1399 (versus), 1359 (s), 1329 (s), 1288 (versus), 1240 (m), 1216 (versus), 1167 (s), 1155 (s), 1059 (versus), 1025 (versus), 1020 (versus), 993 (s), 981 (s), 968 (s), 887 (m), 870 (s), 842 (s), 832 (s), 804 (versus), 775 (s), 731 (m), 652 (versus), 608 (s), 517 (s), 479 (s), 445 (versus), 411 (m).

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.

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

|   | x    | y    | z    | Ueq* |
|---|------|------|------|------|
| O1 | 0.32038 (14) | 0.28041 (15) | 0.2248 (3) | 0.0618 (6) |
| N1 | 0.52051 (15) | 0.08089 (17) | 0.2297 (3) | 0.0456 (6) |
| N2 | 0.61838 (17) | 0.29856 (19) | 0.2153 (3) | 0.0530 (6) |
| N3 | 0.32823 (16) | 0.0787 (2) | 0.2548 (3) | 0.0495 (6) |
| H3N | 0.367 (2) | 0.022 (2) | 0.251 (4) | 0.057 (9)* |
| N4 | 0.04496 (18) | −0.1046 (2) | −0.2659 (4) | 0.0677 (7) |
| C1 | 0.47371 (18) | 0.1855 (2) | 0.2255 (3) | 0.0389 (6) |
| C2 | 0.5226 (2) | 0.2972 (2) | 0.2174 (4) | 0.0477 (7) |
| H2 | 0.4870 | 0.3635 | 0.2132 | 0.057* |
| C3 | 0.6641 (2) | 0.1935 (2) | 0.2189 (4) | 0.0531 (7) |
| H3 | 0.7309 | 0.1925 | 0.2166 | 0.064* |
| C4 | 0.61612 (19) | 0.0861 (2) | 0.2258 (4) | 0.0510 (7) |

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### Atomic displacement parameters (Å²)

|       | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|-------|----------|----------|----------|----------|----------|----------|
| O1    | 0.0615 (13) | 0.0417 (11) | 0.0868 (15) | 0.0116 (10) | 0.0272 (11) | −0.0013 (10) |
| N1    | 0.0459 (13) | 0.0334 (12) | 0.0586 (14) | 0.0012 (10) | 0.0149 (10) | −0.0024 (10) |
| N2    | 0.0553 (15) | 0.0427 (14) | 0.0610 (15) | −0.0100 (11) | 0.0144 (11) | −0.0006 (11) |
| N3    | 0.0421 (14) | 0.0421 (14) | 0.0663 (16) | −0.0008 (11) | 0.0170 (11) | −0.0043 (11) |
| N4    | 0.0590 (16) | 0.0684 (18) | 0.0749 (19) | 0.0011 (13) | 0.0148 (14) | −0.0111 (15) |
| C1    | 0.0441 (14) | 0.0323 (13) | 0.0399 (14) | −0.0006 (11) | 0.0101 (11) | −0.0028 (11) |
| C2    | 0.0560 (18) | 0.0325 (15) | 0.0531 (17) | 0.0008 (12) | 0.0109 (13) | −0.0023 (12) |
| C3    | 0.0488 (17) | 0.0505 (16) | 0.0607 (17) | −0.0050 (14) | 0.0149 (13) | 0.0007 (14) |
| C4    | 0.0496 (16) | 0.0406 (15) | 0.0646 (18) | 0.0044 (13) | 0.0174 (13) | −0.0019 (13) |
| C5    | 0.0501 (16) | 0.0376 (14) | 0.0447 (15) | 0.0009 (13) | 0.0117 (12) | −0.0045 (12) |
| C6    | 0.0471 (16) | 0.0585 (18) | 0.0625 (19) | −0.0012 (13) | 0.0206 (14) | −0.0040 (14) |
| C7    | 0.0321 (13) | 0.0416 (14) | 0.0582 (18) | 0.0048 (11) | 0.0162 (12) | 0.0016 (12) |
| C8    | 0.0442 (15) | 0.0551 (17) | 0.0646 (19) | −0.0022 (13) | 0.0204 (14) | 0.0059 (15) |
| C9    | 0.0589 (19) | 0.084 (2) | 0.056 (2) | 0.0091 (17) | 0.0214 (16) | 0.0066 (17) |
| C10   | 0.0530 (18) | 0.0444 (16) | 0.092 (3) | −0.0008 (14) | 0.0204 (17) | −0.0063 (17) |
| C11   | 0.0457 (15) | 0.0439 (15) | 0.0674 (19) | 0.0043 (13) | 0.0179 (13) | 0.0087 (14) |

### Geometric parameters (Å, °)

|       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|
| O1—C5 | 1.225 (3) | C3—H3 | 0.9300 |
| N1—C4 | 1.333 (3) | C4—H4 | 0.9300 |
| N1—C1 | 1.334 (3) | C6—C7 | 1.504 (3) |
| N2—C3 | 1.332 (3) | C6—H6A | 0.9700 |
| N2—C2 | 1.333 (3) | C6—H6B | 0.9700 |
| N3—C5 | 1.338 (3) | C7—C11 | 1.379 (3) |
| N3—C6 | 1.446 (3) | C7—C8 | 1.379 (4) |
| N3—H3N | 0.83 (3) | C8—C9 | 1.369 (4) |
| N4—C10 | 1.325 (4) | C8—H8 | 0.9300 |
| N4—C9 | 1.337 (4) | C9—H9 | 0.9300 |
| C1—C2 | 1.385 (3) | C10—C11 | 1.381 (4) |
C1—C5 1.500 (3) C10—H10 0.9300
C2—H2 0.9300 C11—H11 0.9300
C3—C4 1.379 (3)

C4—N1—C1 116.2 (2) N3—C6—C7 112.4 (2)
C3—N2—C2 115.2 (2) N3—C6—H6A 109.1
C5—N3—C6 124.1 (2) C7—C6—H6A 109.1
C5—N3—H3N 113.8 (19) N3—C6—H6B 109.1
C6—N3—H3N 121.9 (19) C7—C6—H6B 109.1
C10—N4—C9 115.1 (3) H6A—C6—H6B 107.9
N1—C1—C2 121.3 (2) C11—C7—C8 116.9 (3)
N1—C1—C5 119.0 (2) C11—C7—C6 121.2 (2)
C2—C1—C5 119.6 (2) C8—C7—C6 121.9 (2)
N2—C2—C1 122.8 (2) C9—C8—C7 119.3 (3)
N2—C2—H2 118.6 C9—C8—H8 120.3
C1—C2—H2 118.6 C7—C8—H8 120.3
N2—C3—C4 122.5 (3) N4—C9—C8 124.8 (3)
N2—C3—H3 118.7 N4—C9—H9 117.6
C4—C3—H3 118.7 C8—C9—H9 117.6
N1—C4—C3 121.9 (2) N4—C10—C11 124.4 (3)
N1—C4—H4 119.0 N4—C10—H10 117.8
C3—C4—H4 119.0 C11—C10—H10 117.8
O1—C5—N3 124.2 (2) C7—C11—C10 119.5 (3)
O1—C5—N3 120.9 (2) C7—C11—H11 120.3
N3—C5—C1 114.9 (2) C10—C11—H11 120.3

|   |   |   |   |   |
|---|---|---|---|---|
| C4—N1—C1—C2 | 0.1 (3) |   |   |   |
| C4—N1—C1—C5 | −178.6 (2) |   |   |   |
| C3—N2—C2—C1 | 0.9 (4) |   |   |   |
| N1—C1—C2—N2 | −0.7 (4) |   |   |   |
| C5—C1—C2—N2 | 178.0 (2) |   |   |   |
| C2—N2—C3—C4 | −0.5 (4) |   |   |   |
| C1—N1—C4—C3 | 0.3 (4) |   |   |   |
| N2—C3—C4—N1 | −0.1 (4) |   |   |   |
| C6—N3—C5—O1 | 0.9 (4) |   |   |   |
| C6—N3—C5—C1 | −179.9 (2) |   |   |   |
| N1—C1—C5—O1 | −177.8 (2) |   |   |   |
| C2—C1—C5—O1 | 3.4 (4) |   |   |   |
| N1—C1—C5—N3 | 2.9 (3) |   |   |   |

Hydrogen-bond geometry (Å, °)

|   |   |   |
|---|---|---|
| $D$—$H···A$ | $D$—$H$ | $H···A$ | $D···A$ | $D$—$H···A$ |
| N3—H3N···N1 | 0.83 (3) | 2.27 (3) | 2.713 (3) | 114 (2) |
| N3—H3N···N2i | 0.83 (3) | 2.52 (3) | 3.214 (3) | 142 (2) |
### Supporting Information

|          |        |        |          |      |
|----------|--------|--------|----------|------|
| C2—H2···N1<sup>ii</sup> | 0.93   | 2.47   | 3.315 (3) | 151  |
| C8—H8···O1<sup>iii</sup> | 0.93   | 2.55   | 3.373 (3) | 148  |

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