

The crystal structures of three pyrazine-2,5-dicarboxamides: three-dimensional supramolecular structures

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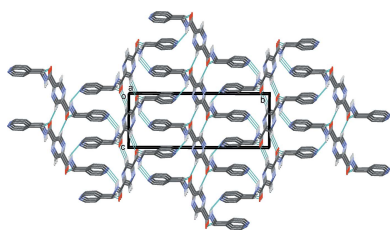
The complete molecules of the title compounds, N^2,N^5 -bis(pyridin-2-ylmethyl)pyrazine-2,5-dicarboxamide, $C_{18}H_{16}N_6O_2$ (I), 3,6-dimethyl- N^2,N^5 -bis(pyridin-2-ylmethyl)pyrazine-2,5-dicarboxamide, $C_{20}H_{20}N_6O_2$ (II), and N^2,N^5 -bis(pyridin-4-ylmethyl)pyrazine-2,5-dicarboxamide, $C_{18}H_{16}N_6O_2$ (III), are generated by inversion symmetry, with the pyrazine rings being located about centres of inversion. Each molecule has an extended conformation with the pyridine rings inclined to the pyrazine ring by $89.17(7)^\circ$ in (I), $75.83(8)^\circ$ in (II) and by $82.71(6)^\circ$ in (III). In the crystal of (I), molecules are linked by N—H \cdots N hydrogen bonds, forming layers lying parallel to the bc plane. The layers are linked by C—H \cdots O hydrogen bonds, forming a three-dimensional supramolecular structure. In the crystal of (II), molecules are also linked by N—H \cdots N hydrogen bonds, forming layers lying parallel to the $(10\bar{1})$ plane. As in (I), the layers are linked by C—H \cdots O hydrogen bonds, forming a three-dimensional supramolecular structure. In the crystal of (III), molecules are again linked by N—H \cdots N hydrogen bonds, but here form corrugated sheets lying parallel to the bc plane. Within the sheets, neighbouring pyridine rings are linked by offset π - π interactions [intercentroid distance = $3.739(1)$ Å]. The sheets are linked by C—H \cdots O hydrogen bonds, forming a three-dimensional supramolecular structure. Compound (I) crystallizes in the monoclinic space group $P2_1/c$. Another monoclinic polymorph, space group $C2/c$, has been reported on by Cockriel *et al.* [*Inorg. Chem. Commun.* (2008), **11**, 1–4]. The molecular structures of the two polymorphs are compared.

1. Chemical context

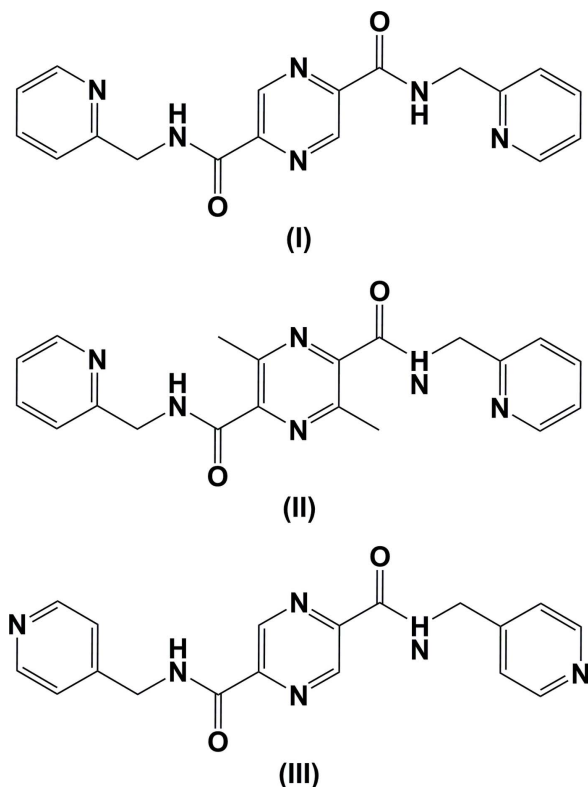
The title compounds are part of a series of pyrazine mono- and di- and tetrakis-carboxamide derivatives synthesized to study their coordination chemistry with essentially first-row transition metals (Cati, 2002). Compound (I) crystallizes in the monoclinic space group $P2_1/c$. Another monoclinic polymorph, space group $C2/c$, has been described by Cockriel *et al.* (2008).

2. Structural commentary

The molecular structures of the title compounds, (I), (II) and (III), are illustrated in Figs. 1, 2 and 3, respectively. The whole molecule of each compound is generated by inversion symmetry, with the pyrazine rings being located about centers of inversion. Each molecule has an extended conformation with the pyridine rings inclined to the pyrazine ring by $89.17(7)^\circ$ in (I), by $75.83(8)^\circ$ in (II) and by $82.71(6)^\circ$ in (III). The methylcarboxamide units (C4—N2—C3=O1) are



inclined to the pyrazine ring by 4.24 (9), 3.13 (10) and 9.32 (8) $^{\circ}$ in (I), (II) and (III), respectively.



In the monoclinic $C2/c$ polymorph of (I) (Cockriel *et al.*, 2008), the whole molecule is also generated by inversion

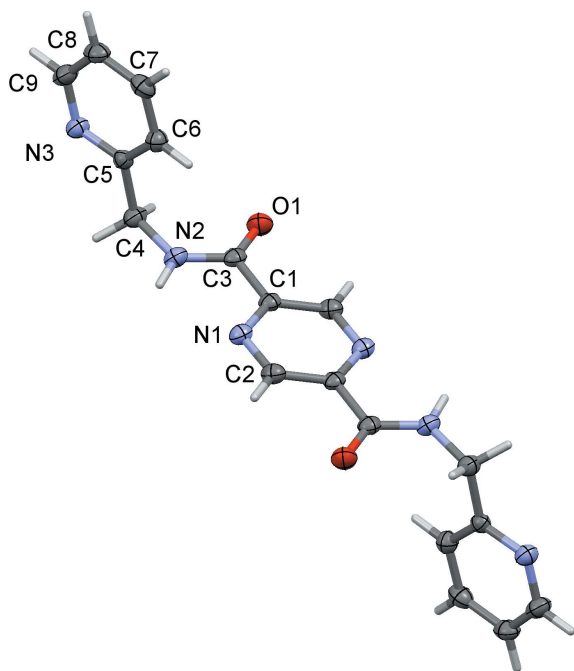


Figure 1
A view of the molecular structure of compound (I), with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. The unlabelled atoms are related to the labelled atoms by inversion symmetry (symmetry operation: $-x, -y, -z + 2$).

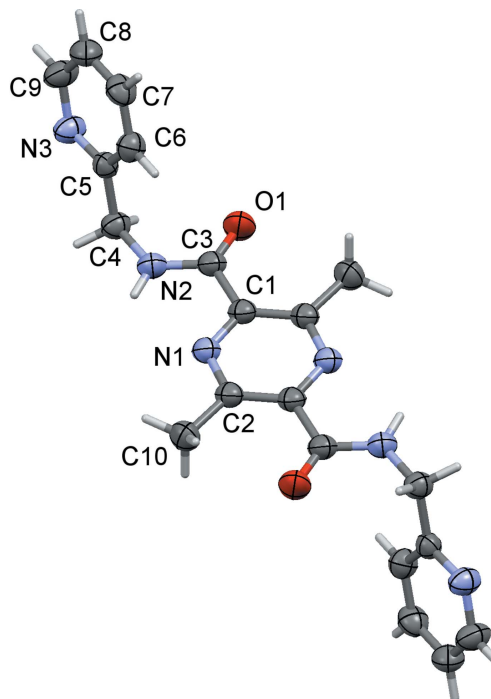


Figure 2
A view of the molecular structure of compound (II), with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. The unlabelled atoms are related to the labelled atoms by inversion symmetry (symmetry operation: $-x, -y, -z$).

symmetry (Fig. 4). However, here the molecule is almost planar with the pyridine rings being inclined to the pyrazine ring by only 5.70 (7) $^{\circ}$. The pyridine ring is orientated in such a manner that the NH hydrogen atom forms short contacts with both the adjacent pyrazine and pyridine N atoms, as shown in Fig. 4. The carbonyl O atom also accepts a short contact from a pyrazine H atom (Fig. 4).

3. Supramolecular features

In the crystal of (I), molecules are linked by N—H \cdots N hydrogen bonds, forming layers lying parallel to the bc plane

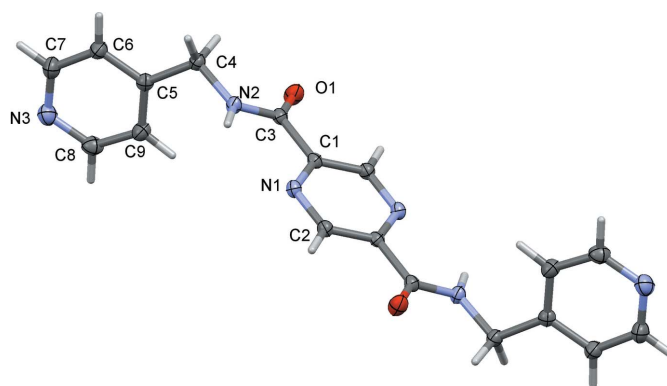


Figure 3
A view of the molecular structure of compound (III), with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. The unlabelled atoms are related to the labelled atoms by inversion symmetry (symmetry operation: $-x + 1, -y + 1, -z + 2$).

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2N\cdots N3^i$	0.88 (2)	2.209 (17)	3.0657 (18)	164 (2)
$C7-H7\cdots O1^{ii}$	0.95	2.53	3.292 (2)	137

 Symmetry codes: (i) $-x, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x - 1, y - \frac{1}{2}, -z + \frac{3}{2}$.

Table 2
 Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2N\cdots N3^i$	0.85 (2)	2.35 (2)	3.097 (2)	147.4 (18)
$C7-H7\cdots O1^{ii}$	0.93	2.59	3.263 (2)	130

 Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$.

Table 3
 Hydrogen-bond geometry (Å, °) for (III).

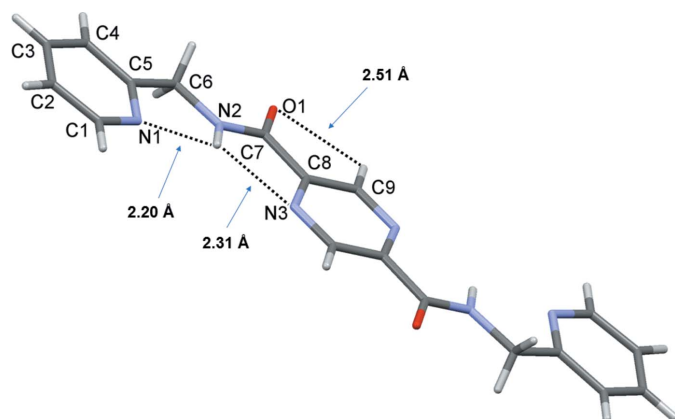
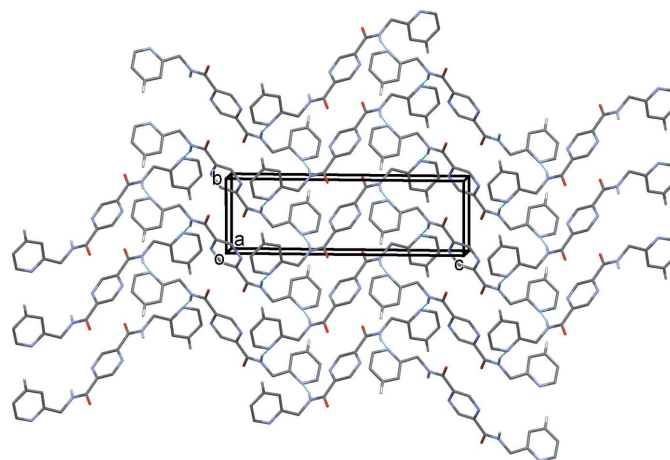
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2N\cdots N3^i$	0.93 (2)	2.50 (2)	3.2420 (19)	137.5 (16)
$C2-H2\cdots O1^{ii}$	0.95	2.33	3.2411 (18)	160
$C4-H4B\cdots O1^{iii}$	0.99	2.49	3.4636 (18)	166

 Symmetry codes: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $x, y, z + 1$; (iii) $x - 1, y, z$.

(Table 1 and Fig. 5). The layers are linked by $C-H\cdots O$ hydrogen bonds, forming a three-dimensional supramolecular structure (Table 1 and Fig. 6)

In the crystal of (II), molecules are linked by $N-H\cdots N$ hydrogen bonds, forming layers lying parallel to the $(10\bar{1})$ plane (Table 2 and Fig. 7). As in the crystal of (I), the layers are linked by $C-H\cdots O$ hydrogen bonds, forming a three-dimensional supramolecular structure (Table 2 and Fig. 8)

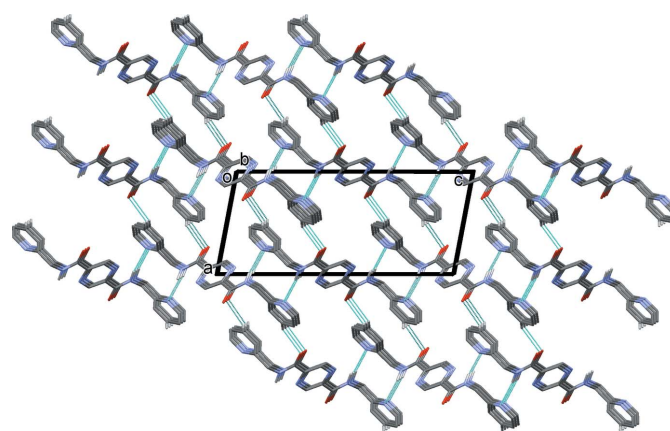
In the crystal of (III), molecules are linked by $N-H\cdots N$ hydrogen bonds, forming corrugated sheets lying parallel to the bc plane (Table 3 and Fig. 9). The sheets are linked by $C-H\cdots O$ hydrogen bonds, forming a three-dimensional supramolecular structure (Table 3 and Fig. 10). Within the sheets,


Figure 4
 A view of the molecular structure of the monoclinic $C2/c$ polymorph (Cockriel *et al.*, 2008) of compound (I), with the atom labelling. The unlabelled atoms are related to the labelled atoms by inversion symmetry (symmetry operation: $-x + \frac{1}{2}, -y - \frac{1}{2}, -z + 1$).

Figure 5
 A view along the a axis of the crystal pack of compound (I). The $N-H\cdots N$ hydrogen bonds are shown as dashed lines (see Table 1). For clarity, in this and subsequent figures, only the H atoms involved in hydrogen bonding have been included.

neighbouring pyridine rings are linked by offset $\pi-\pi$ interactions [$Cg2\cdots Cg2^{iv} = 3.739$ (1) Å, $Cg2$ is the centroid of the pyridine ring (N3/C5–C9), $\alpha = 1.85$ (7)°, interplanar distances = 3.525 (1) and 3.552 (1) Å, slippage = 1.168 Å; symmetry code: (iv) $x + 1, -y + \frac{1}{2}, z + \frac{1}{2}$].

4. Database survey

A search of the Cambridge Structural Database (Version 5.38, update February 2017; Groom *et al.*, 2016) for pyrazine-2,5-dicarboxamides yielded three hits, *viz.* N,N' -bis(4-pentylphenyl)pyrazine-2,5-dicarboxamide (CSD refcode: DABDOC; Zhang *et al.*, 2015), N,N' -diphenylpyrazine-2,5-dicarboxamide (HIYKEH; Cheng *et al.*, 2014), and the monoclinic $C2/c$ polymorph of compound (I) (AFAPOV; Cockriel *et al.*, 2008), mentioned above. All three compounds possess inversion symmetry and HIYKEH, like APAPOV, has an almost planar conformation (*cf.* Fig. 4).


Figure 6
 A view along the b axis of the crystal pack of compound (I). The hydrogen bonds are shown as dashed lines (see Table 1).

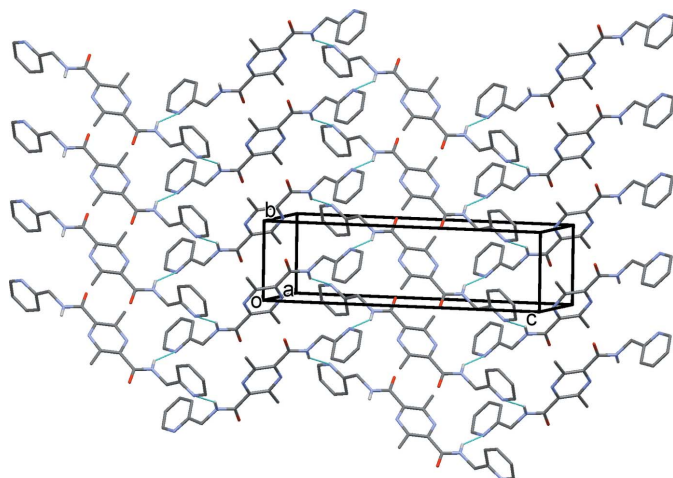


Figure 7
A view along the normal to plane $(10\bar{1})$, of the crystal pack of compound (II). The N—H \cdots N hydrogen bonds are shown as dashed lines (see Table 2).

5. Synthesis and crystallization

Pyrazine 2,5-dicarboxylic acid was prepared by oxidation of 2,5-dimethylpyrazine with selenium dioxide (Schut *et al.*, 1961).

Dimethyl 3,6-dimethylpyrazine-2,5-dicarboxylate was prepared following reported procedures (Takeuchi *et al.*, 1990; Wang, 1996).

Dimethyl pyrazine-2,5-dicarboxylate was obtained following the procedure described by (Schut *et al.*, 1961). A mixture of anhydrous pyrazine-2,5-dicarboxylic acid (5 g, 30 mmol), absolute methanol (190 ml) and 1.5 ml (*ca* 3 g) of conc. sulfuric acid were refluxed until a clear solution was obtained (*ca* 9 h). After standing overnight at 268 K, the crystalline product formed was filtered off, washed with ice-cold methanol (2×20 ml) then dried over P_2O_5 [yield 90%, m.p. 441 (1) K].

Note: Both pyrazine 2,5-dicarboxylic acid and dimethyl pyrazine-2,5-dicarboxylate are also available commercially.

Compound (I): was prepared by refluxing dimethyl pyrazine-2,5-dicarboxylate (1.00 g, 5 mmol) and an excess of 2-(aminomethyl)pyridine (1.55g, 14.3 mmol) in 30 ml of

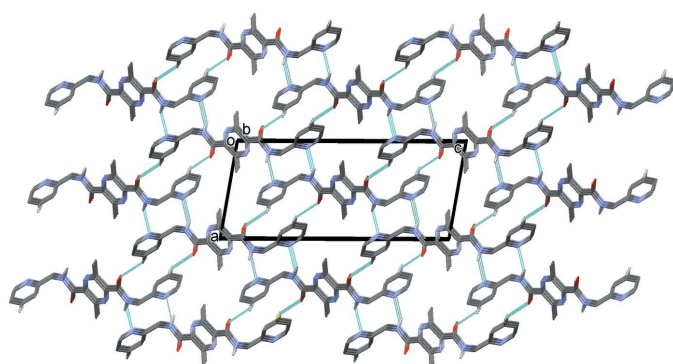


Figure 8
A view along the *b* axis of the crystal pack of compound (II). The hydrogen bonds are shown as dashed lines (see Table 2).

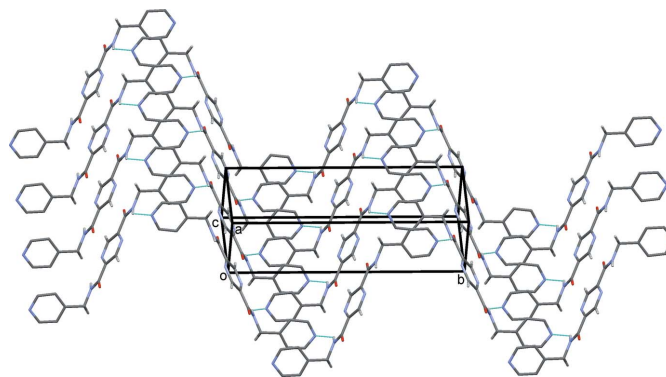


Figure 9
A partial view, normal to plane $(10\bar{1})$, of the crystal pack of compound (III). The N—H \cdots N hydrogen bonds are shown as dashed lines (see Table 3).

methanol in a two-necked flask (100 ml). After 150 min a precipitate appeared, and after refluxing for 5 h the suspension was cooled to room temperature. A white solid was filtered off and washed with 10 ml of cold methanol. It was then recrystallized from dichloromethane solution to give colourless plate-like crystals of (I) suitable for X-ray diffraction analysis (yield 81%, m.p. 479 K).

Spectroscopic and analytical data:

^1H NMR (400 MHz, $\text{DMSO-}d_6$): 9.51 (*t*, 1H, $J_{\text{hg}} = 5.9$, Hh); 9.28 (*s*, 1H, Hl = Hn); 8.54 (*ddd*, 1H, $J_{\text{bc}} = 4.8$, $J_{\text{bd}} = 1.8$, $J_{\text{be}} = 0.8$, Hb); 7.76 (*td*, 1H, $J_{\text{dc}} = 7.7$, $J_{\text{db}} = 1.8$, Hd); 7.38 (*d*, 1H, $J_{\text{ed}} = 7.8$, He); 7.28 (*m*, 1H, Hc); 4.68 (*d*, 2H, $J_{\text{gh}} = 5.9$, Hg).

^{13}C NMR (400 MHz, $\text{DMSO-}d_6$): 163.4, 158.5, 149.7, 147.4, 143.0, 137.6, 123.1, 122.0, 45.2.

IR (KBr pellet, cm^{-1}): 3335 (*s*), 3055 (*m*), 2916 (*w*), 1683 (*vs*), 1603 (*s*), 1593 (*s*), 1572 (*s*), 1522 (*vs*), 1483 (*s*), 1464 (*vs*), 1436 (*vs*), 1364 (*m*), 1328 (*s*), 1296 (*m*), 1255 (*m*), 1242 (*m*), 1210 (*m*), 1182 (*m*), 1148 (*m*), 1048 (*m*), 1028 (*m*), 1024 (*m*), 999 (*m*), 943 (*w*), 903 (*s*), 759 (*vs*), 728 (*m*), 668 (*m*), 506 (*s*), 461 (*s*).

Analysis for $\text{C}_{18}\text{H}_{16}\text{N}_6\text{O}_2$ ($M_r = 348.36$ g mol $^{-1}$). Calculated (%) C: 62.06, H: 4.63, N: 24.12. Found (%) C: 62.00, H: 4.67, N: 24.30.

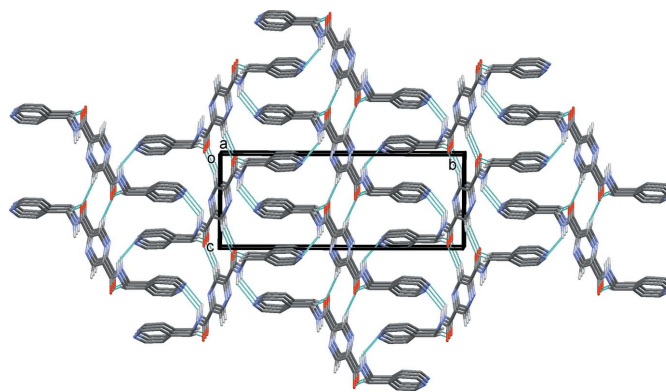


Figure 10
A view along the *a* axis of the crystal pack of compound (III). The hydrogen bonds are shown as dashed lines (see Table 3).

Table 4
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	C ₁₈ H ₁₆ N ₆ O ₂	C ₂₀ H ₂₀ N ₆ O ₂	C ₁₈ H ₁₆ N ₆ O ₂
<i>M_r</i>	348.37	376.42	348.37
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>	Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>
Temperature (K)	153	293	153
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.0769 (9), 5.6076 (7), 18.3724 (18)	8.7271 (5), 5.2950 (4), 20.1403 (13)	5.8663 (6), 18.7539 (17), 7.2943 (8)
β (°)	100.781 (12)	99.834 (6)	101.606 (12)
<i>V</i> (Å ³)	817.44 (16)	917.01 (11)	786.08 (14)
<i>Z</i>	2	2	2
Radiation type	Mo <i>K</i> α	Cu <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.10	0.75	0.10
Crystal size (mm)	0.45 × 0.25 × 0.15	0.46 × 0.19 × 0.19	0.35 × 0.30 × 0.25
Data collection			
Diffractometer	Stoe <i>IPDS</i> 1	Stoe–Siemens AED2 four-circle	Stoe <i>IPDS</i> 1
Absorption correction	Multi-scan (<i>MULABS</i> ; Spek, 2009)	Multi-scan (<i>MULABS</i> ; Spek, 2009)	Multi-scan (<i>MULABS</i> ; Spek, 2009)
<i>T</i> _{min} – <i>T</i> _{max}	0.987, 1.000	0.955, 1.000	0.962, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	5998, 1574, 1024	2576, 1345, 1226	5980, 1513, 1259
<i>R</i> _{int}	0.037	0.015	0.026
θ _{max} (°)	25.9	59.6	25.9
(sin θ/λ) _{max} (Å ⁻¹)	0.615	0.559	0.615
Refinement			
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.032, 0.076, 0.87	0.035, 0.095, 1.05	0.036, 0.097, 1.08
No. of reflections	1574	1345	1513
No. of parameters	123	133	122
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	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.16, -0.15	0.18, -0.12	0.44, -0.19

Computer programs: *EXPOSE*, *CELL* and *INTEGRATE* in *IPDS-I* (Stoe & Cie, 2004), *STADIA* (Stoe & Cie, 1997), *X-RED* (Stoe & Cie, 1997), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* and *SHELXL2016* (Sheldrick, 2015), *PLATON* (Spek, 2009), *Mercury* (Macrae *et al.*, 2008) and *pubCIF* (Westrip, 2010).

Compound (II): was prepared by refluxing dimethyl 3,6-dimethylpyrazine-2,5-dicarboxylate (1.5 g, 5.92 mmol) and an excess of 2-(aminomethyl)pyridine (1.63 g, 15 mmol) in 25 ml of methanol, in a two-necked flask (100 ml) for 55 h. A colourless precipitate formed and this suspension was then cooled to room temperature. The solid that had formed was filtered off and washed with 10 ml of cold methanol. It was then recrystallized from ethyl acetate solution to give colourless rod-like crystals of (II) [yield 90%, m.p. 470 K].

Spectroscopic and analytical data:

¹H NMR (400 MHz, DMSO-*d*₆): 9.39 (*t*, 1H, *J*_{hg} = 6.1, Hh); 8.54 (*ddd*, 1H, *J*_{bc} = 4.8, *J*_{bd} = 1.8, *J*_{be} = 0.9, Hb); 7.79 (*td*, 1H, *J*_{dc} = 7.7, *J*_{db} = 1.8, Hd); 7.37 (*d*, 1H, *J*_{ed} = 7.9, He); 7.29 (*m*, 1H, Hc); 4.61 (*d*, 2H, *J*_{gh} = 6.1, Hg); 2.79 (*s*, 3H, CH₃).

¹³C NMR (400 MHz, DMSO-*d*₆): 165.5, 158.9, 149.8, 149.7, 145.3, 137.7, 123.1, 121.9, 45.2, 22.8.

IR (KBr pellet, cm⁻¹): 3310 (*s*), 3090 (*m*), 3055 (*m*), 3011 (*m*), 2904 (*m*), 1673 (*vs*), 1609 (*m*), 1592 (*vs*), 1569 (*s*), 1506 (*vs*), 1474 (*vs*), 1435 (*vs*), 1411 (*vs*), 1372 (*m*), 1352 (*s*), 1275 (*s*), 1243 (*s*), 1185 (*s*), 1158 (*s*), 1092 (*m*), 1050 (*m*), 1033 (*w*), 1015 (*s*), 995 (*s*), 971 (*m*), 959 (*w*), 888 (*w*), 833 (*m*), 770 (*m*), 759 (*s*), 715 (*s*), 640 (*m*), 556 (*m*), 526 (*s*), 463 (*m*), 447 (*m*).

Analysis for C₂₀H₂₀N₆O₂ (*M_r* = 376.42 g mol⁻¹). Calculated (%) C: 63.82, H: 5.36, N: 22.33. Found (%) C: 63.74, H: 5.46, N: 22.42.

Compound (III): was prepared by heating to reflux a mixture of dimethyl pyrazine-2,5-dicarboxylate (1.00 g, 5 mmol) with an excess of 4-(aminomethyl)pyridine (1.55g, 14.3 mmol) in 35 ml of methanol in a two-necked flask (100 ml). After 6 h the white solid that had formed was filtered off and washed with 10 ml of cold methanol. It was then recrystallized from dichloromethane solution to give colourless block-like crystals of (III) [yield 85%, m.p. 530 K (degradation)].

Spectroscopic and analytical data:

¹H NMR (400 MHz, DMSO-*d*₆): 9.80 (*t*, 1H, *J*_{hg} = 6.3, Hh); 9.25 (*s*, 1H, Hn = Hl); 8.50 (*dd*, 2H, *J*_{ba} = 4.5, *J*_{be} = 1.5, Hb = Hd); 7.33 (*dd*, 2H, *J*_{ab} = 4.5, *J*_{eb} = 1.5, Ha = He); 4.55 (*d*, 2H, *J*_{gh} = 6.3, Hg).

¹³C NMR (400 MHz, DMSO-*d*₆): 163.7, 150.4, 148.8, 147.4, 143.0, 123.1, 42.5.

IR (KBr pellet, cm⁻¹): 3348 (*s*), 3089 (*w*), 3073 (*w*), 3032 (*w*), 2997 (*w*), 2934 (*w*), 2359 (*w*), 1949 (*w*), 1712 (*m*), 1662 (*vs*), 1604 (*s*), 1561 (*s*), 1533 (*vs*), 1496 (*w*), 1472 (*m*), 1427 (*s*), 1418 (*vs*), 1373 (*m*), 1317 (*w*), 1282 (*s*), 1233 (*w*), 1220 (*w*), 1204 (*w*), 1171 (*s*), 1135 (*w*), 1067 (*w*), 1028 (*m*), 991 (*s*), 970 (*w*), 824 (*m*), 777 (*m*), 726 (*w*), 671 (*m*), 662 (*m*), 607 (*w*), 511 (*m*), 457 (*m*).

Analysis for C₁₈H₁₆N₆O₂·0.5CH₃OH (*M₂* = 364.39 g mol⁻¹). Calculated (%) C: 60.98, H: 4.98, N: 23.06. Found (%) C: 61.12, H: 4.83, N: 22.85.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. Intensity data for (I) and (III) were measured at 153 K on a one-circle image-plate diffractometer, while for (II) intensity data were measured at 293 K on a four-circle diffractometer. For all three compounds, 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: C–H = 0.95–0.99 Å for (I) and (III) with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$; C–H = 0.93–0.96 Å for (II), with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C-methyl})$ and $1.2U_{\text{eq}}(\text{C})$ for other H atoms.

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References

Cati, D. (2002). PhD thesis, University of Neuchâtel, Switzerland.

- Cheng, N., Yan, Q., Liu, S. & Zhao, D. (2014). *CrystEngComm*, **16**, 4265–4273.
- Cockriel, D. L., McClain, J. M., Patel, K. C., Ullom, R., Hasley, T. R., Archibald, S. J. & Hubin, T. J. (2008). *Inorg. Chem. Commun.* **11**, 1–4.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Schut, W. J., Mager, H. I. X. & Berends, W. (1961). *Recl Trav. Chim. Pays Bas*, **80**, 391–398.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Stoe & Cie (1997). *STADIA Software*. Stoe & Cie GmbH, Darmstadt, Germany.
- Stoe & Cie (2004). *IPDSI Bedienungshandbuch*. Stoe & Cie GmbH, Darmstadt, Germany.
- Takeuchi, R., Suzuki, K. & Sato, N. (1990). *Synthesis*, **1990**, 923–924.
- Wang, Y. (1996). PhD thesis, University of Neuchâtel, Switzerland.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Zhang, Q.-C., Takeda, T., Hoshino, N., Noro, S., Nakamura, T. & Akutagawa, T. (2015). *Cryst. Growth Des.* **15**, 5705–5711.

supporting information

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The crystal structures of three pyrazine-2,5-dicarboxamides: three-dimensional supramolecular structures

Dilovan S. Cati and Helen Stoeckli-Evans

Computing details

Data collection: *EXPOSE* in *IPDS-I* (Stoe & Cie, 2004) for (I), (III); *STADIA* (Stoe & Cie, 1997) for (II). Cell refinement: *CELL* in *IPDS-I* (Stoe & Cie, 2004) for (I), (III); *STADIA* (Stoe & Cie, 1997) for (II). Data reduction: *INTEGRATE* in *IPDS-I* (Stoe & Cie, 2004) for (I), (III); *X-RED* (Stoe & Cie, 1997) for (II). For all compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015). Molecular graphics: *Mercury* (Macrae *et al.*, 2008) for (I); *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008) for (II), (III). Software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *pubCIF* (Westrip, 2010) for (I), (III); *SHELXL2016* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *pubCIF* (Westrip, 2010) for (II).

(I) *N*²,*N*⁵-Bis(pyridin-2-ylmethyl)pyrazine-2,5-dicarboxamide

Crystal data

$C_{18}H_{16}N_6O_2$	$F(000) = 364$
$M_r = 348.37$	$D_x = 1.415 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 8.0769 (9) \text{ \AA}$	Cell parameters from 3344 reflections
$b = 5.6076 (7) \text{ \AA}$	$\theta = 2.3\text{--}25.9^\circ$
$c = 18.3724 (18) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$\beta = 100.781 (12)^\circ$	$T = 153 \text{ K}$
$V = 817.44 (16) \text{ \AA}^3$	Plate, colourless
$Z = 2$	$0.45 \times 0.25 \times 0.15 \text{ mm}$

Data collection

Stoe IPDS 1	5998 measured reflections
diffractometer	1574 independent reflections
Radiation source: fine-focus sealed tube	1024 reflections with $I > 2\sigma(I)$
Plane graphite monochromator	$R_{\text{int}} = 0.037$
φ rotation scans	$\theta_{\text{max}} = 25.9^\circ$, $\theta_{\text{min}} = 2.3^\circ$
Absorption correction: multi-scan	$h = -9 \rightarrow 9$
(MULABS; Spek, 2009)	$k = -6 \rightarrow 6$
$T_{\text{min}} = 0.987$, $T_{\text{max}} = 1.000$	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	$S = 0.87$
Least-squares matrix: full	1574 reflections
$R[F^2 > 2\sigma(F^2)] = 0.032$	123 parameters
$wR(F^2) = 0.076$	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

$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.16 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.15 \text{ e } \text{\AA}^{-3}$
Extinction correction: SHELXL2016
(Sheldrick, 2015),
 $F_c^* = kFc[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.029 (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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.05799 (15)	0.0574 (2)	0.93513 (7)	0.0261 (3)
N2	-0.05730 (16)	0.4484 (2)	0.85602 (7)	0.0274 (3)
H2N	0.031 (2)	0.366 (3)	0.8485 (10)	0.045 (5)*
N3	-0.26574 (14)	0.7526 (2)	0.68676 (7)	0.0274 (3)
O1	-0.24558 (13)	0.51737 (18)	0.93146 (6)	0.0336 (3)
C1	-0.06037 (17)	0.1872 (2)	0.95909 (8)	0.0232 (3)
C2	0.11771 (18)	-0.1299 (3)	0.97651 (8)	0.0262 (4)
H2A	0.201781	-0.226769	0.961478	0.031*
C3	-0.13034 (17)	0.4004 (3)	0.91401 (8)	0.0253 (4)
C4	-0.10976 (18)	0.6452 (3)	0.80607 (8)	0.0283 (4)
H4A	-0.009417	0.709655	0.789038	0.034*
H4B	-0.155051	0.773295	0.833863	0.034*
C5	-0.24122 (16)	0.5825 (3)	0.73894 (8)	0.0223 (3)
C6	-0.33024 (18)	0.3704 (3)	0.73168 (9)	0.0278 (4)
H6	-0.308875	0.252378	0.769361	0.033*
C7	-0.45098 (18)	0.3331 (3)	0.66858 (9)	0.0317 (4)
H7	-0.513660	0.188834	0.662344	0.038*
C8	-0.47904 (19)	0.5068 (3)	0.61521 (9)	0.0323 (4)
H8	-0.561978	0.485946	0.571644	0.039*
C9	-0.38401 (19)	0.7125 (3)	0.62623 (9)	0.0332 (4)
H9	-0.403298	0.832226	0.589013	0.040*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0263 (6)	0.0271 (7)	0.0233 (7)	0.0005 (5)	0.0001 (5)	0.0007 (6)
N2	0.0282 (7)	0.0282 (7)	0.0240 (7)	0.0038 (6)	0.0001 (6)	0.0040 (6)
N3	0.0286 (7)	0.0269 (7)	0.0256 (7)	0.0020 (6)	0.0024 (6)	0.0033 (6)
O1	0.0294 (6)	0.0338 (6)	0.0371 (7)	0.0068 (5)	0.0051 (5)	0.0049 (5)
C1	0.0216 (7)	0.0249 (8)	0.0210 (8)	-0.0027 (6)	-0.0018 (6)	-0.0015 (6)
C2	0.0244 (7)	0.0269 (8)	0.0257 (8)	0.0023 (6)	0.0006 (6)	-0.0024 (7)

C3	0.0229 (7)	0.0262 (8)	0.0240 (8)	-0.0019 (6)	-0.0026 (6)	-0.0006 (7)
C4	0.0298 (8)	0.0260 (8)	0.0265 (9)	-0.0019 (6)	-0.0012 (7)	0.0036 (7)
C5	0.0207 (7)	0.0243 (8)	0.0222 (8)	0.0032 (6)	0.0046 (6)	0.0001 (6)
C6	0.0283 (8)	0.0270 (8)	0.0278 (9)	-0.0013 (6)	0.0048 (6)	0.0022 (7)
C7	0.0247 (8)	0.0341 (9)	0.0365 (10)	-0.0053 (7)	0.0058 (7)	-0.0071 (8)
C8	0.0245 (8)	0.0433 (10)	0.0267 (9)	0.0011 (7)	-0.0014 (6)	-0.0057 (8)
C9	0.0332 (9)	0.0380 (9)	0.0258 (9)	0.0062 (7)	-0.0014 (7)	0.0049 (7)

Geometric parameters (Å, °)

N1—C2	1.3330 (19)	C4—C5	1.5107 (19)
N1—C1	1.3397 (18)	C4—H4A	0.9900
N2—C3	1.338 (2)	C4—H4B	0.9900
N2—C4	1.4475 (19)	C5—C6	1.383 (2)
N2—H2N	0.879 (19)	C6—C7	1.384 (2)
N3—C5	1.3405 (18)	C6—H6	0.9500
N3—C9	1.3424 (19)	C7—C8	1.370 (2)
O1—C3	1.2290 (17)	C7—H7	0.9500
C1—C2 ⁱ	1.387 (2)	C8—C9	1.380 (2)
C1—C3	1.503 (2)	C8—H8	0.9500
C2—H2A	0.9500	C9—H9	0.9500
C2—N1—C1	116.42 (13)	C5—C4—H4B	108.6
C3—N2—C4	122.52 (13)	H4A—C4—H4B	107.6
C3—N2—H2N	120.6 (12)	N3—C5—C6	122.56 (13)
C4—N2—H2N	116.8 (12)	N3—C5—C4	113.93 (12)
C5—N3—C9	117.41 (13)	C6—C5—C4	123.51 (13)
N1—C1—C2 ⁱ	121.83 (13)	C5—C6—C7	118.86 (14)
N1—C1—C3	117.97 (13)	C5—C6—H6	120.6
C2 ⁱ —C1—C3	120.21 (13)	C7—C6—H6	120.6
N1—C2—C1 ⁱ	121.75 (13)	C8—C7—C6	119.23 (14)
N1—C2—H2A	119.1	C8—C7—H7	120.4
C1 ⁱ —C2—H2A	119.1	C6—C7—H7	120.4
O1—C3—N2	124.66 (14)	C7—C8—C9	118.44 (14)
O1—C3—C1	120.38 (14)	C7—C8—H8	120.8
N2—C3—C1	114.96 (13)	C9—C8—H8	120.8
N2—C4—C5	114.69 (12)	N3—C9—C8	123.49 (15)
N2—C4—H4A	108.6	N3—C9—H9	118.3
C5—C4—H4A	108.6	C8—C9—H9	118.3
N2—C4—H4B	108.6		
C2—N1—C1—C2 ⁱ	0.0 (2)	C9—N3—C5—C6	1.1 (2)
C2—N1—C1—C3	179.79 (12)	C9—N3—C5—C4	-178.26 (13)
C1—N1—C2—C1 ⁱ	0.0 (2)	N2—C4—C5—N3	-168.30 (13)
C4—N2—C3—O1	-1.0 (2)	N2—C4—C5—C6	12.3 (2)
C4—N2—C3—C1	179.29 (12)	N3—C5—C6—C7	-0.9 (2)
N1—C1—C3—O1	175.99 (13)	C4—C5—C6—C7	178.46 (14)
C2 ⁱ —C1—C3—O1	-4.2 (2)	C5—C6—C7—C8	0.0 (2)

N1—C1—C3—N2	−4.33 (18)	C6—C7—C8—C9	0.6 (2)
C2 ⁱ —C1—C3—N2	175.43 (12)	C5—N3—C9—C8	−0.5 (2)
C3—N2—C4—C5	−92.36 (17)	C7—C8—C9—N3	−0.3 (2)

Symmetry code: (i) $-x, -y, -z+2$.

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2N ⁱⁱ —N3 ⁱⁱ	0.88 (2)	2.209 (17)	3.0657 (18)	164 (2)
C7—H7 ⁱⁱⁱ —O1 ⁱⁱⁱ	0.95	2.53	3.292 (2)	137

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

(II) 3,6-Dimethyl- N^2, N^5 -bis(pyridin-2-ylmethyl)pyrazine-2,5-dicarboxamide

Crystal data

$C_{20}H_{20}N_6O_2$

$M_r = 376.42$

Monoclinic, $P2_1/n$

$a = 8.7271$ (5) Å

$b = 5.2950$ (4) Å

$c = 20.1403$ (13) Å

$\beta = 99.834$ (6)°

$V = 917.01$ (11) Å³

$Z = 2$

$F(000) = 396$

$D_x = 1.363$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54186$ Å

Cell parameters from 22 reflections

$\theta = 20.4$ – 32.0 °

$\mu = 0.75$ mm⁻¹

$T = 293$ K

Rod, colourless

$0.46 \times 0.19 \times 0.19$ mm

Data collection

Stoe–Siemens AED2 four-circle diffractometer

Radiation source: fine-focus sealed tube

Plane graphite monochromator

$\omega/2\theta$ scans

Absorption correction: multi-scan (MULABS; Spek, 2009)

$T_{\min} = 0.955$, $T_{\max} = 1.000$

2576 measured reflections

1345 independent reflections

1226 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$

$\theta_{\max} = 59.6$ °, $\theta_{\min} = 4.5$ °

$h = -9 \rightarrow 9$

$k = 0 \rightarrow 5$

$l = -22 \rightarrow 22$

2 standard reflections every 60 min

intensity decay: 2%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.095$

$S = 1.05$

1345 reflections

133 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

$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 0.2943P]$

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

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

$\Delta\rho_{\max} = 0.18$ e Å⁻³

$\Delta\rho_{\min} = -0.12$ e Å⁻³

Extinction correction: SHELXL2016

(Sheldrick, 2015),

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

Extinction coefficient: 0.0124 (10)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	1.12510 (14)	0.4700 (3)	0.90448 (6)	0.0615 (4)
N1	0.88491 (14)	0.9651 (3)	0.94504 (6)	0.0422 (4)
N2	0.89518 (17)	0.6199 (3)	0.85116 (7)	0.0466 (4)
H2N	0.818 (2)	0.714 (4)	0.8529 (10)	0.061 (6)*
N3	0.94177 (16)	0.3148 (3)	0.69204 (7)	0.0503 (4)
C1	1.01225 (18)	0.8206 (3)	0.95440 (8)	0.0399 (4)
C2	0.86917 (18)	1.1468 (3)	0.98964 (8)	0.0408 (4)
C3	1.01729 (18)	0.6201 (3)	0.90156 (8)	0.0432 (4)
C4	0.87726 (19)	0.4317 (3)	0.79852 (8)	0.0453 (4)
H4A	0.767587	0.416493	0.779865	0.054*
H4B	0.911490	0.270168	0.818461	0.054*
C5	0.96522 (17)	0.4847 (3)	0.74167 (8)	0.0381 (4)
C6	1.06331 (19)	0.6880 (3)	0.74049 (9)	0.0466 (5)
H6	1.074867	0.807192	0.774909	0.056*
C7	1.14401 (19)	0.7128 (4)	0.68778 (9)	0.0514 (5)
H7	1.210827	0.848639	0.686234	0.062*
C8	1.1248 (2)	0.5356 (4)	0.63781 (9)	0.0529 (5)
H8	1.179711	0.545797	0.602164	0.064*
C9	1.0223 (2)	0.3422 (4)	0.64172 (9)	0.0577 (5)
H9	1.008001	0.223016	0.607303	0.069*
C10	0.7223 (2)	1.3002 (4)	0.97432 (9)	0.0539 (5)
H10A	0.672121	1.267830	0.928884	0.081*
H10B	0.747288	1.476475	0.979389	0.081*
H10C	0.653830	1.254180	1.004892	0.081*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0552 (8)	0.0691 (9)	0.0594 (8)	0.0208 (7)	0.0074 (6)	-0.0159 (7)
N1	0.0423 (8)	0.0466 (8)	0.0392 (7)	0.0049 (6)	0.0106 (6)	-0.0015 (6)
N2	0.0454 (8)	0.0516 (9)	0.0439 (8)	0.0066 (7)	0.0105 (7)	-0.0085 (7)
N3	0.0541 (9)	0.0501 (9)	0.0494 (8)	-0.0114 (7)	0.0165 (7)	-0.0128 (7)
C1	0.0403 (9)	0.0436 (10)	0.0380 (8)	0.0016 (7)	0.0132 (7)	0.0003 (7)
C2	0.0405 (9)	0.0431 (9)	0.0406 (9)	0.0035 (7)	0.0125 (7)	0.0016 (7)
C3	0.0435 (9)	0.0483 (10)	0.0403 (9)	0.0035 (8)	0.0141 (7)	-0.0024 (8)
C4	0.0480 (9)	0.0456 (10)	0.0437 (9)	-0.0039 (8)	0.0119 (7)	-0.0069 (8)
C5	0.0342 (8)	0.0384 (9)	0.0410 (9)	0.0028 (7)	0.0047 (6)	-0.0026 (7)
C6	0.0479 (10)	0.0429 (10)	0.0486 (10)	-0.0050 (8)	0.0071 (8)	-0.0064 (8)
C7	0.0442 (10)	0.0527 (11)	0.0577 (11)	-0.0086 (8)	0.0101 (8)	0.0047 (9)

C8	0.0491 (10)	0.0644 (12)	0.0482 (10)	-0.0025 (9)	0.0167 (8)	0.0022 (9)
C9	0.0668 (12)	0.0616 (13)	0.0495 (10)	-0.0104 (10)	0.0232 (9)	-0.0164 (9)
C10	0.0476 (10)	0.0573 (12)	0.0553 (11)	0.0116 (9)	0.0047 (8)	-0.0047 (9)

Geometric parameters (Å, °)

O1—C3	1.2255 (19)	C4—H4B	0.9700
N1—C1	1.336 (2)	C5—C6	1.378 (2)
N1—C2	1.339 (2)	C6—C7	1.377 (2)
N2—C3	1.340 (2)	C6—H6	0.9300
N2—C4	1.444 (2)	C7—C8	1.365 (3)
N2—H2N	0.85 (2)	C7—H7	0.9300
N3—C5	1.335 (2)	C8—C9	1.371 (3)
N3—C9	1.336 (2)	C8—H8	0.9300
C1—C2 ⁱ	1.404 (2)	C9—H9	0.9300
C1—C3	1.509 (2)	C10—H10A	0.9600
C2—C10	1.504 (2)	C10—H10B	0.9600
C4—C5	1.510 (2)	C10—H10C	0.9600
C4—H4A	0.9700		
C1—N1—C2	119.67 (13)	N3—C5—C4	114.19 (14)
C3—N2—C4	121.93 (15)	C6—C5—C4	123.79 (14)
C3—N2—H2N	120.4 (14)	C7—C6—C5	119.25 (16)
C4—N2—H2N	116.7 (14)	C7—C6—H6	120.4
C5—N3—C9	117.48 (15)	C5—C6—H6	120.4
N1—C1—C2 ⁱ	121.60 (14)	C8—C7—C6	119.26 (16)
N1—C1—C3	115.29 (14)	C8—C7—H7	120.4
C2 ⁱ —C1—C3	123.11 (14)	C6—C7—H7	120.4
N1—C2—C1 ⁱ	118.73 (14)	C7—C8—C9	118.03 (16)
N1—C2—C10	115.57 (14)	C7—C8—H8	121.0
C1 ⁱ —C2—C10	125.69 (15)	C9—C8—H8	121.0
O1—C3—N2	122.72 (16)	N3—C9—C8	123.91 (17)
O1—C3—C1	122.48 (15)	N3—C9—H9	118.0
N2—C3—C1	114.80 (14)	C8—C9—H9	118.0
N2—C4—C5	115.02 (14)	C2—C10—H10A	109.5
N2—C4—H4A	108.5	C2—C10—H10B	109.5
C5—C4—H4A	108.5	H10A—C10—H10B	109.5
N2—C4—H4B	108.5	C2—C10—H10C	109.5
C5—C4—H4B	108.5	H10A—C10—H10C	109.5
H4A—C4—H4B	107.5	H10B—C10—H10C	109.5
N3—C5—C6	122.01 (15)		
C2—N1—C1—C2 ⁱ	0.3 (3)	C9—N3—C5—C6	2.7 (2)
C2—N1—C1—C3	179.38 (14)	C9—N3—C5—C4	-176.51 (16)
C1—N1—C2—C1 ⁱ	-0.3 (2)	N2—C4—C5—N3	-177.14 (14)
C1—N1—C2—C10	179.58 (15)	N2—C4—C5—C6	3.6 (2)
C4—N2—C3—O1	3.9 (3)	N3—C5—C6—C7	-2.3 (3)
C4—N2—C3—C1	-176.38 (14)	C4—C5—C6—C7	176.86 (15)

N1—C1—C3—O1	-178.22 (15)	C5—C6—C7—C8	0.1 (3)
C2 ⁱ —C1—C3—O1	0.9 (3)	C6—C7—C8—C9	1.4 (3)
N1—C1—C3—N2	2.0 (2)	C5—N3—C9—C8	-1.1 (3)
C2 ⁱ —C1—C3—N2	-178.88 (15)	C7—C8—C9—N3	-1.0 (3)
C3—N2—C4—C5	-83.2 (2)		

Symmetry code: (i) $-x+2, -y+2, -z+2$.

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>
N2—H2N...N3 ⁱⁱ	0.85 (2)	2.35 (2)	3.097 (2)	147.4 (18)
C7—H7...O1 ⁱⁱⁱ	0.93	2.59	3.263 (2)	130

Symmetry codes: (ii) $-x+3/2, y+1/2, -z+3/2$; (iii) $-x+5/2, y+1/2, -z+3/2$.

(III) *N*²,*N*⁵-Bis(pyridin-4-ylmethyl)pyrazine-2,5-dicarboxamide

Crystal data

C₁₈H₁₆N₆O₂

M_r = 348.37

Monoclinic, *P*2₁/*c*

a = 5.8663 (6) Å

b = 18.7539 (17) Å

c = 7.2943 (8) Å

β = 101.606 (12)°

V = 786.08 (14) Å³

Z = 2

F(000) = 364

D_x = 1.472 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 5301 reflections

θ = 2.2–25.9°

μ = 0.10 mm⁻¹

T = 153 K

Block, colourless

0.35 × 0.30 × 0.25 mm

Data collection

Stoe IPDS 1

diffractometer

Radiation source: fine-focus sealed tube

Plane graphite monochromator

φ rotation scans

Absorption correction: multi-scan

(MULABS; Spek, 2009)

*T*_{min} = 0.962, *T*_{max} = 1.000

5980 measured reflections

1513 independent reflections

1259 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.026

θ_{max} = 25.9°, θ_{min} = 2.2°

h = -7→7

k = -22→23

l = -8→8

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.036

wR(*F*²) = 0.097

S = 1.08

1513 reflections

122 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

w = 1/[σ²(*F*_o²) + (0.0502*P*)² + 0.2467*P*]

where *P* = (*F*_o² + 2*F*_c²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.44 e Å⁻³

Δρ_{min} = -0.19 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.30168 (19)	0.46198 (6)	1.02233 (16)	0.0173 (3)
N2	−0.00374 (19)	0.41317 (6)	0.72012 (17)	0.0187 (3)
H2N	−0.029 (3)	0.4166 (10)	0.841 (3)	0.039 (5)*
N3	−0.2298 (2)	0.15345 (7)	0.55300 (19)	0.0293 (3)
O1	0.24963 (17)	0.44020 (6)	0.53216 (14)	0.0265 (3)
C1	0.3536 (2)	0.47275 (7)	0.85410 (18)	0.0160 (3)
C2	0.4500 (2)	0.48929 (7)	1.16888 (19)	0.0178 (3)
H2	0.420845	0.482665	1.291218	0.021*
C3	0.1942 (2)	0.44098 (7)	0.68574 (19)	0.0172 (3)
C4	−0.1807 (2)	0.38348 (7)	0.5713 (2)	0.0203 (3)
H4A	−0.148718	0.399204	0.449379	0.024*
H4B	−0.334049	0.403073	0.582431	0.024*
C5	−0.1943 (2)	0.30298 (7)	0.57217 (19)	0.0188 (3)
C6	−0.4033 (3)	0.26981 (8)	0.4972 (2)	0.0243 (3)
H6	−0.538854	0.297195	0.450754	0.029*
C7	−0.4112 (3)	0.19603 (8)	0.4913 (2)	0.0300 (4)
H7	−0.555967	0.174192	0.439677	0.036*
C8	−0.0300 (3)	0.18638 (8)	0.6274 (2)	0.0263 (3)
H8	0.102255	0.157690	0.674601	0.032*
C9	−0.0045 (2)	0.25969 (8)	0.6396 (2)	0.0233 (3)
H9	0.141680	0.280149	0.693639	0.028*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0187 (6)	0.0146 (5)	0.0189 (6)	−0.0010 (4)	0.0041 (5)	−0.0002 (4)
N2	0.0183 (6)	0.0194 (6)	0.0182 (6)	−0.0038 (5)	0.0033 (5)	−0.0020 (5)
N3	0.0346 (7)	0.0212 (6)	0.0303 (7)	−0.0015 (5)	0.0023 (6)	−0.0005 (6)
O1	0.0264 (5)	0.0345 (6)	0.0193 (5)	−0.0081 (4)	0.0063 (4)	−0.0033 (4)
C1	0.0172 (6)	0.0121 (6)	0.0185 (7)	0.0017 (5)	0.0032 (5)	−0.0002 (5)
C2	0.0203 (7)	0.0159 (7)	0.0175 (7)	−0.0007 (5)	0.0044 (5)	0.0007 (5)
C3	0.0189 (6)	0.0131 (6)	0.0194 (7)	0.0004 (5)	0.0030 (5)	−0.0003 (5)
C4	0.0192 (7)	0.0184 (7)	0.0216 (7)	−0.0015 (5)	0.0001 (5)	−0.0012 (6)
C5	0.0206 (7)	0.0195 (7)	0.0168 (7)	−0.0013 (5)	0.0049 (5)	−0.0015 (5)
C6	0.0209 (7)	0.0217 (7)	0.0283 (8)	−0.0012 (6)	0.0005 (6)	−0.0006 (6)
C7	0.0292 (8)	0.0225 (8)	0.0358 (9)	−0.0061 (6)	0.0009 (7)	−0.0015 (6)
C8	0.0280 (8)	0.0242 (8)	0.0256 (8)	0.0049 (6)	0.0029 (6)	−0.0011 (6)
C9	0.0197 (7)	0.0246 (8)	0.0248 (7)	−0.0014 (6)	0.0022 (6)	−0.0029 (6)

Geometric parameters (Å, °)

N1—C2	1.3372 (18)	C4—C5	1.5120 (19)
N1—C1	1.3378 (18)	C4—H4A	0.9900
N2—C3	1.3417 (18)	C4—H4B	0.9900
N2—C4	1.4536 (17)	C5—C9	1.385 (2)
N2—H2N	0.93 (2)	C5—C6	1.386 (2)
N3—C7	1.334 (2)	C6—C7	1.385 (2)
N3—C8	1.339 (2)	C6—H6	0.9500
O1—C3	1.2278 (17)	C7—H7	0.9500
C1—C2 ⁱ	1.3928 (19)	C8—C9	1.384 (2)
C1—C3	1.5085 (18)	C8—H8	0.9500
C2—H2	0.9500	C9—H9	0.9500
C2—N1—C1	116.35 (12)	C5—C4—H4B	108.7
C3—N2—C4	121.62 (12)	H4A—C4—H4B	107.6
C3—N2—H2N	117.3 (12)	C9—C5—C6	117.45 (13)
C4—N2—H2N	120.9 (12)	C9—C5—C4	123.19 (12)
C7—N3—C8	115.74 (13)	C6—C5—C4	119.32 (12)
N1—C1—C2 ⁱ	122.28 (12)	C7—C6—C5	118.82 (14)
N1—C1—C3	117.96 (12)	C7—C6—H6	120.6
C2 ⁱ —C1—C3	119.75 (12)	C5—C6—H6	120.6
N1—C2—C1 ⁱ	121.37 (13)	N3—C7—C6	124.63 (14)
N1—C2—H2	119.3	N3—C7—H7	117.7
C1 ⁱ —C2—H2	119.3	C6—C7—H7	117.7
O1—C3—N2	124.33 (13)	N3—C8—C9	123.95 (14)
O1—C3—C1	120.85 (12)	N3—C8—H8	118.0
N2—C3—C1	114.80 (12)	C9—C8—H8	118.0
N2—C4—C5	114.18 (11)	C8—C9—C5	119.40 (13)
N2—C4—H4A	108.7	C8—C9—H9	120.3
C5—C4—H4A	108.7	C5—C9—H9	120.3
N2—C4—H4B	108.7		
C2—N1—C1—C2 ⁱ	-0.5 (2)	N2—C4—C5—C9	-29.1 (2)
C2—N1—C1—C3	178.30 (11)	N2—C4—C5—C6	152.96 (13)
C1—N1—C2—C1 ⁱ	0.5 (2)	C9—C5—C6—C7	-0.8 (2)
C4—N2—C3—O1	-4.5 (2)	C4—C5—C6—C7	177.20 (14)
C4—N2—C3—C1	177.11 (11)	C8—N3—C7—C6	1.0 (2)
N1—C1—C3—O1	-169.52 (12)	C5—C6—C7—N3	-0.1 (3)
C2 ⁱ —C1—C3—O1	9.29 (19)	C7—N3—C8—C9	-1.0 (2)
N1—C1—C3—N2	8.95 (17)	N3—C8—C9—C5	0.1 (2)
C2 ⁱ —C1—C3—N2	-172.24 (12)	C6—C5—C9—C8	0.8 (2)
C3—N2—C4—C5	106.64 (15)	C4—C5—C9—C8	-177.11 (14)

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N2—H2N \cdots N3 ⁱⁱ	0.93 (2)	2.50 (2)	3.2420 (19)	137.5 (16)
C2—H2 \cdots O1 ⁱⁱⁱ	0.95	2.33	3.2411 (18)	160
C4—H4B \cdots O1 ^{iv}	0.99	2.49	3.4636 (18)	166

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