



Crystal structures and Hirshfeld surface analyses of two new tetrakis-substituted pyrazines and a degradation product

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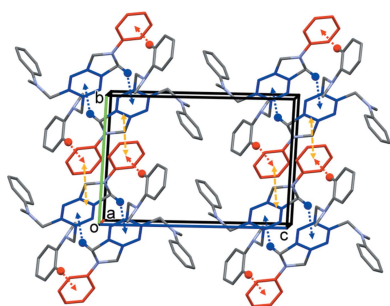
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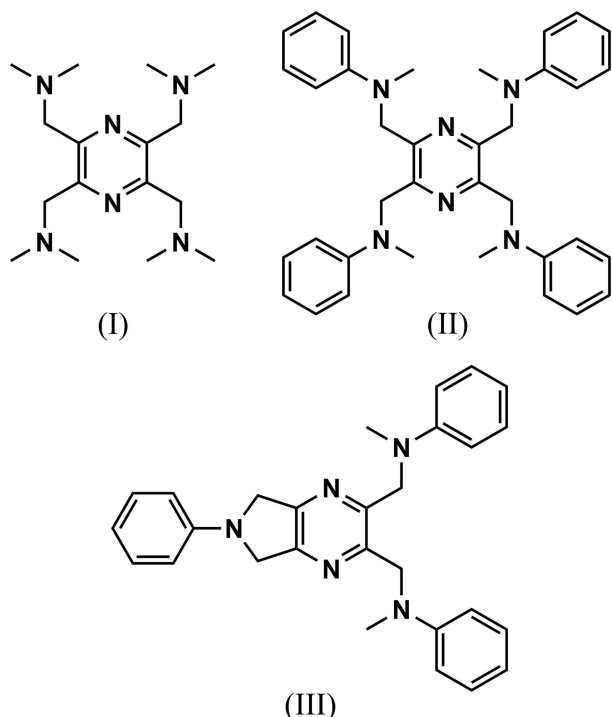
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The two new tetrakis-substituted pyrazines, 1,1',1'',1'''-(pyrazine-2,3,5,6-tetrayl)tetrakis(*N,N*-dimethylmethanamine), C₁₆H₃₂N₆, (I) and *N,N',N'',N'''*-[pyrazine-2,3,5,6-tetrayltetrakis(methylene)]tetrakis(*N*-methylaniline), C₃₆H₄₀N₆, (II), both crystallize with half a molecule in the asymmetric unit; the whole molecules are generated by inversion symmetry. There are weak intramolecular C—H···N hydrogen bonds present in both molecules and in (II) the pendant *N*-methylaniline rings are linked by a C—H··· π interaction. The degradation product, *N,N'*-[(6-phenyl-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyrazine-2,3-diyl)bis(methylene)]bis(*N*-methylaniline), C₂₈H₂₉N₅, (III), was obtained several times by reacting (II) with different metal salts. Here, the 6-phenyl ring is almost coplanar with the planar pyrrolo[3,4-*b*]pyrazine unit (r.m.s. deviation = 0.029 Å), with a dihedral angle of 4.41 (10)° between them. The two *N*-methylaniline rings are inclined to the planar pyrrolo[3,4-*b*]pyrazine unit by 88.26 (10) and 89.71 (10)°, and to each other by 72.56 (13)°. There are also weak intramolecular C—H···N hydrogen bonds present involving the pyrazine ring and the two *N*-methylaniline groups. In the crystal of (I), there are no significant intermolecular contacts present, while in (II) molecules are linked by a pair of C—H··· π interactions, forming chains along the *c*-axis direction. In the crystal of (III), molecules are linked by two pairs of C—H··· π interactions, forming inversion dimers, which in turn are linked by offset π – π interactions [intercentroid distance = 3.8492 (19) Å], forming ribbons along the *b*-axis direction.

1. Chemical context

Tetrakis-substituted pyrazines, which are potential bis-tridentate ligands, have been used in coordination chemistry since the 1980's, to form not only mononuclear and binuclear complexes but also multi-dimensional coordination polymers. A search of the Cambridge Structural Database (CSD, Version 5.41, last update November 2019; Groom *et al.*, 2016) reveals that the principal tetrakis-substituted pyrazine ligands that have been used are 2,3,5,6-tetrakis(pyridin-2-yl)pyrazine, which was first synthesized by Goodwin & Lions (1959), and 2,3,5,6-pyrazinetetracarboxylic acid, which was first synthesized by Wolff at the end of the 19th century (Wolff, 1887, 1893). Since then the coordination chemistry of only a small number of tetrakis-substituted pyrazines has been studied, for example tetrakis(aminomethyl)pyrazine (Ferigo *et al.*, 1994) and, more recently, the new ligand 2,3,5,6-tetrakis(4-carboxyphenyl)pyrazine, which has been shown to be extremely successful in forming metal–organic frameworks (Jiang *et al.*, 2017; Wang *et al.*, 2019).





In our search for new tetrakis-substituted pyrazine ligands (Tesouro Vallina, 2001), *viz.* potential bis-tridentate ligands, the title compounds, 1,1',1'',1'''-(pyrazine-2,3,5,6-tetrayl) tetrakis(*N,N*-dimethylmethanamine) (I) and *N,N',N'',N'''*-[pyrazine-2,3,5,6-tetrayl tetrakis(methylene)] tetrakis(*N*-methylaniline) (II) were synthesized. During attempts to form transition-metal complexes of (II), the degradation product, *N,N'*-[(6-phenyl-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyrazine-2,3-diyl)bis(methylene)]bis(*N*-methylaniline) (III) was often formed. Herein, we describe their molecular and crystal structures, together with the Hirshfeld surface analysis of their crystal packing.

2. Structural commentary

The molecular structure of compound (I) is illustrated in Fig. 1. The molecule possesses inversion symmetry with the pyrazine ring being located about a center of symmetry. The adjacent dimethylmethanamine substituents, in positions 2,3 (and 5,6), are directed above and below the plane of the pyrazine ring. There is a short intramolecular C3—H3A···N3ⁱ contact on either side of the molecule [symmetry code: (i) $-x, -y, -z + 1$], linking the two dimethylmethanamine substituents (Fig. 1 and Table 1).

The molecular structure of compound (II) is illustrated in Fig. 2. This molecule also possesses inversion symmetry with the pyrazine ring being located about a center of symmetry. Again the adjacent methylaniline substituents, in positions 2,3 (and 5,6), are directed above and below the plane of the pyrazine ring. Rings C4—C9 and C12—C17 are inclined to the pyrazine ring by 63.62 (10) and 86.83 (10)°, respectively, and to each other by 78.28 (11)°. There are short intramolecular C5—H5···N1 contacts on either side of the molecule invol-

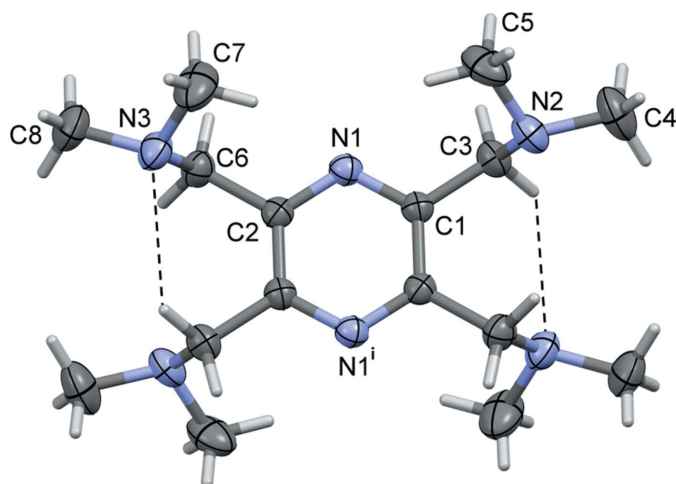


Figure 1
A view of the molecular structure of compound (I), with atom labelling [symmetry code: (i) $-x, -y, -z + 1$]. Displacement ellipsoids are drawn at the 30% probability level. Intramolecular C—H···N interactions (Table 1) are shown as dashed lines.

ving a methylaniline ring and the adjacent pyrazine N atom, and the methylaniline substituents in positions 2,6 (and 3,5)

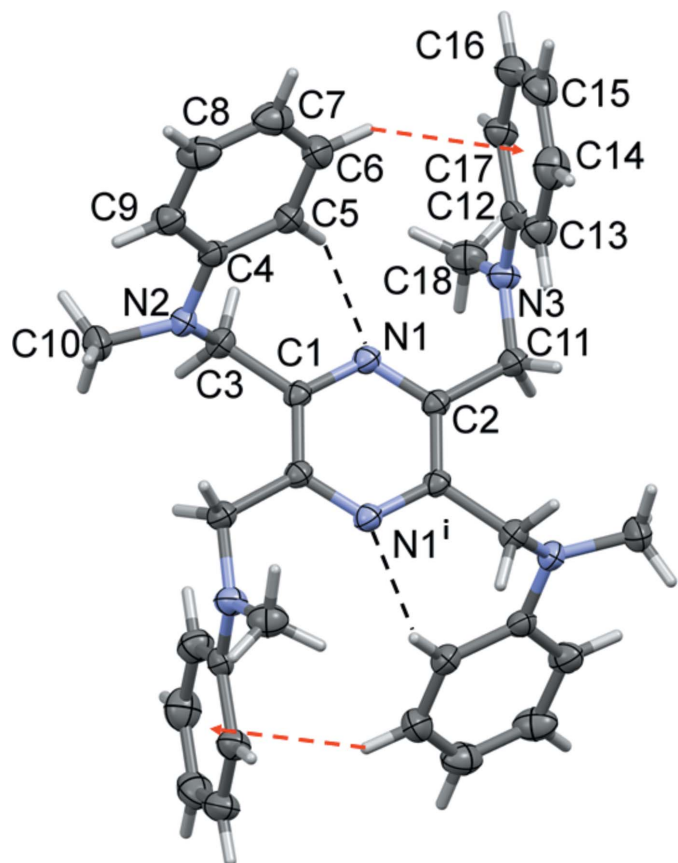


Figure 2
A view of the molecular structure of compound (II), with atom labelling [symmetry code: (i) $-x + 1, -y + 1, -z + 2$]. Displacement ellipsoids are drawn at the 30% probability level. Intramolecular C—H···N interactions (Table 2) are shown as dashed lines and the intramolecular C—H··· π interactions (Table 2) as red dashed arrows.

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

<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>
C3—H3A···N3 ⁱ	0.97	2.62	3.261 (4)	124

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

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

*Cg*2 and *Cg*3 are the centroids of rings C4–C9 and C12–C17, respectively.

<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>
C5—H5···N1	0.93	2.50	3.331 (3)	149
C6—H6··· <i>Cg</i> 3	0.93	2.99	3.804 (3)	147
C3—H3A··· <i>Cg</i> 2 ⁱ	0.97	2.83	3.561 (2)	133

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

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

*Cg*2 and *Cg*3 are the centroids of rings N1/N2/C1–C4 and C7–C12, respectively.

<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>
C15—H15···N4	0.93	2.61	3.542 (3)	175
C28—H28B···N2	0.96	2.59	3.323 (3)	133
C6—H6B··· <i>Cg</i> 2 ⁱ	0.97	2.82	3.601 (2)	138
C23—H23··· <i>Cg</i> 3 ⁱ	0.93	2.97	3.881 (3)	168

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

are linked by an intramolecular C6—H6··· π interaction (Fig. 2 and Table 2).

The molecular structure of compound (III) is illustrated in Fig. 3. One side of the molecule has been transformed into a pyrrolo unit fused to the pyrazine ring. The 6-phenyl ring (C7–C12) is almost coplanar with the planar pyrrolo[3,4-*b*]pyrazine unit (N1–N3/C1–C6; r.m.s. deviation = 0.029 Å), forming a dihedral angle of 4.41 (10)°. On the other side of the molecule, the two adjacent *N*-methylaniline rings (C14–C19 and C22–C27) are inclined to the planar pyrrolo[3,4-*b*]pyrazine unit by

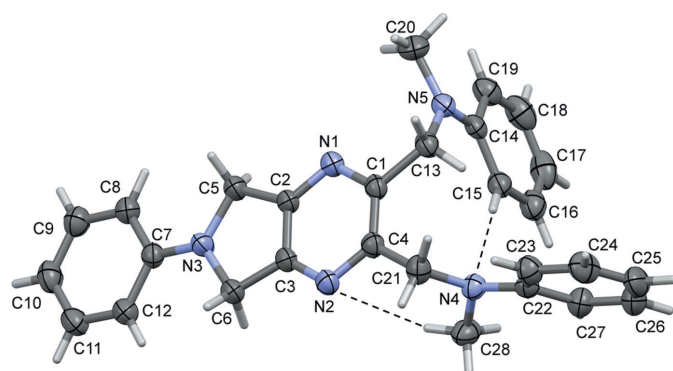


Figure 3
A view of the molecular structure of compound (III), with atom labelling. Displacement ellipsoids are drawn at the 30% probability level. Intramolecular C—H···N interactions (Table 3) are shown as dashed lines.

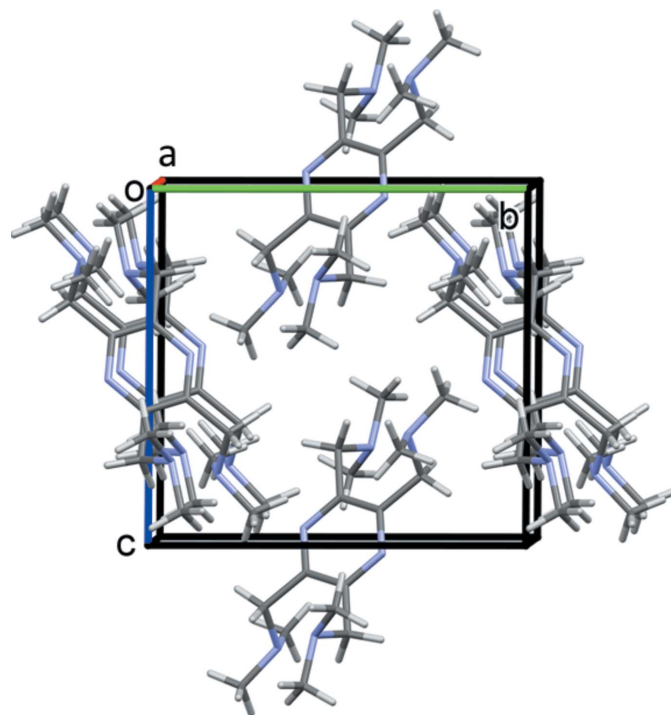


Figure 4
A view along the *a* axis of the crystal packing of compound (I).

88.26 (10) and 89.71 (10)°, and to each other by 72.56 (13)°. There are also weak intramolecular C—H···N hydrogen bonds present involving the pyrazine ring and the two *N*-methylaniline groups (Fig. 3 and Table 3).

3. Supramolecular features

In the crystal of (I), there are no significant intermolecular interactions present (Fig. 4).

In the crystal of (II), molecules are linked by a pair of C—H··· π interactions, forming chains that propagate along the [001] direction (Fig. 5 and Table 2).

In the crystal of (III), molecules are linked by two pairs of C—H··· π interactions, forming inversion dimers. Offset π – π interactions link the dimers to form ribbons propagating along the [010] direction; see Fig. 6 and Table 3. The offset π – π interaction, *Cg*3···*Cg*6ⁱⁱ, where *Cg*3 and *Cg*6 are, respectively, the centroids of the phenyl ring (C7–C12) and the pyrrolo[3,4-*b*]pyrazine ring system, has a centroid–centroid distance of 3.8492 (14) Å, $\alpha = 4.41$ (10)°, interplanar distances of

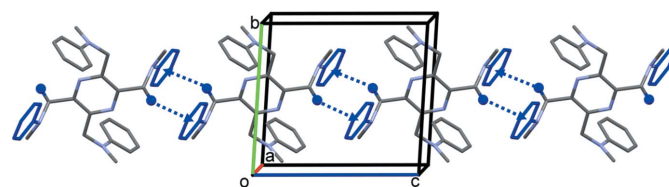
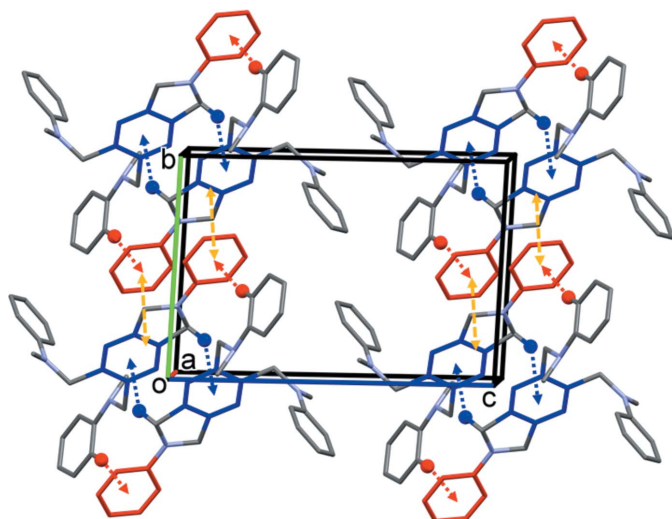


Figure 5
A view along the *a* axis of the crystal packing of compound (II). The C3—H3A··· π interactions (Table 2) are shown as blue dashed arrows, and for clarity, only H atom H3A (blue) has been included.


Figure 6

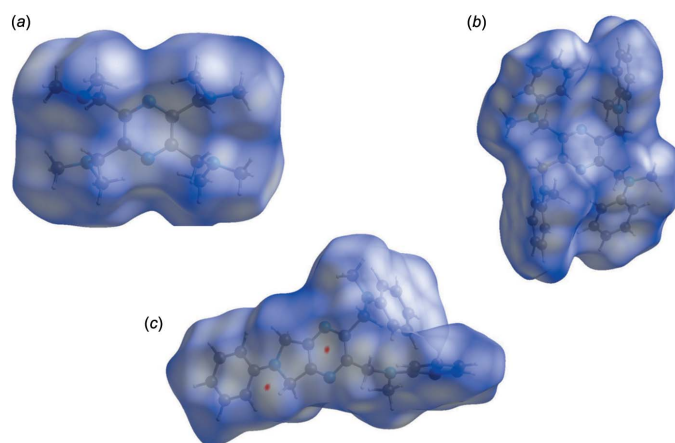
A view along the a axis of the crystal packing of compound (III). The $C-H\cdots\pi$ interactions (Table 3) are shown as blue and red dashed arrows. For clarity, only the H atoms H6B (blue) and H23 (red) have been included. The offset π - π interactions are shown as orange dashed double arrows.

3.6495 (14) and 3.5490 (7) Å, with an offset of 1.49 Å [symmetry code: (ii) $-x + 1, -y + 1, -z$].

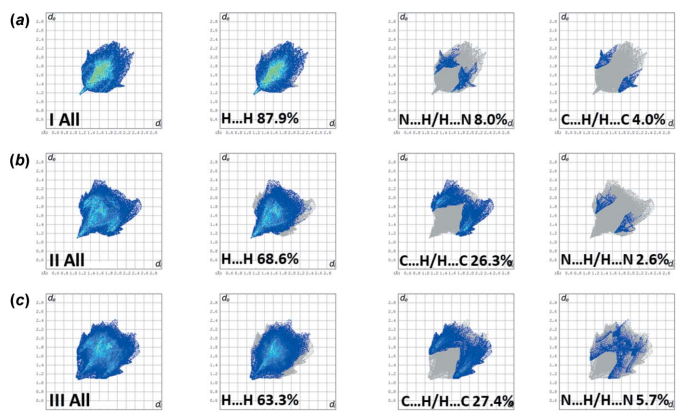
4. Hirshfeld surface analysis and two-dimensional fingerprint plots

The Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) and the associated two-dimensional fingerprint plots (McKinnon *et al.*, 2007) were performed with *Crystal-Explorer17* (Turner *et al.*, 2017).

The Hirshfeld surfaces are colour-mapped with the normalized contact distance, d_{norm} , from red (distances shorter


Figure 7

(a) The Hirshfeld surface of compound (I), mapped over d_{norm} in the colour range -0.7519 to 1.6997 a.u., (b) the Hirshfeld surface of compound (II), mapped over d_{norm} in the colour range -0.7519 to 1.6997 a.u. and (c) the Hirshfeld surface of compound (III), mapped over d_{norm} in the colour range -0.7519 to 1.6997 a.u..


Figure 8

(a) The full two-dimensional fingerprint plot for compound (I), and fingerprint plots delineated into $H\cdots H$, $N\cdots H/H\cdots N$ and $C\cdots H/H\cdots C$ contacts, (b) the full two-dimensional fingerprint plot for compound (II), and fingerprint plots delineated into $H\cdots H$, $C\cdots H/H\cdots C$ and $N\cdots H/H\cdots N$ contacts and (c) the full two-dimensional fingerprint plot for compound (III), and fingerprint plots delineated into $H\cdots H$, $C\cdots H/H\cdots C$ and $N\cdots H/H\cdots N$ contacts.

than the sum of the van der Waals radii) through white to blue (distances longer than the sum of the van der Waals radii). The Hirshfeld surfaces (HS) of the title compounds, mapped over d_{norm} , are given in Fig. 7. It is evident from Figs. 7a and 7b that there are no contact distances shorter than the sum of the van der Waals radii in the crystals of either compounds (I) or (II). For compound (III) (Fig. 7c), two small red spots indicate the presence of weak $C\cdots H$ contacts (see Table 3).

The two-dimensional fingerprint plots for the title compounds are given in Fig. 8. They reveal, as expected, that the principal contributions to the overall surface involve $H\cdots H$ contacts at 87.9% for (I) (Fig. 8a), 68.6% for (II) (Fig. 8b), and 63.3% for (III) (Fig. 8c). The second most important contribution to the HS for compound (I) is from the $N\cdots H/H\cdots N$ contacts at 8.0%; for compounds (II) and (III) the second most significant contributions are from the $C\cdots H/H\cdots C$ contacts at 26.3 and 27.4%, respectively. For compound (I), the third most important contribution to the HS is from the $C\cdots H/H\cdots C$ contacts at 4.0%, while for compounds (II) and (III) it is from the $N\cdots H/H\cdots N$ contacts at 2.6 and 5.7%, respectively. All other atom \cdots atom contacts contribute less than 2% to the HS for all three compounds.

5. Database survey

A search of the CSD (Version 5.41, last update November 2019; Groom *et al.*, 2016) for the structure of 2,3,5,6-tetrakis(pyridin-2-yl)pyrazine gave 289 hits, of which 91 structures are polymeric. The first polymeric compound to be reported in 1995 was for a trinuclear cobalt(II) one-dimensional coordination polymer, *catena*-[bis(μ_2 -chloro)acetonitriletetrachloro-[2,3,5,6-tetrakis(2-pyridyl)pyrazine]tricobalt(II)] (CSD ref-code TUPWAC; Constable *et al.*, 1995).

A search for the structure of 2,3,5,6-pyrazinetetracarboxylic acid gave 92 hits, of which 64 are polymeric. Here, the first

polymeric compound to be reported in 1986 was for a binuclear iron(II) polymer chain, *catena*-[μ_2 -(2,5-dicarboxypyrazine-3,6-dicarboxylato-*N,O*)-*trans*-diaquadiiron(II)] dihydrate (DUWROC; Marioni *et al.*, 1986).

A search for the structure of tetrakis(aminomethyl)pyrazine yielded only eight hits, of which five compounds are polymeric; see for example *catena*-[μ_2 -[tetrakis(aminomethyl)pyrazine-*N,N',N''*]manganese dichloride dihydrate] (PITXEV; Ferigo *et al.*, 1994), and *catena*-[[μ_2 -2,3,5,6-tetrakis(aminomethyl)pyrazine]bis(μ_2 -chloro)dichlorodicopper hydrate] (PITXIZ; Ferigo *et al.*, 1994).

Recently a new ligand, 2,3,5,6-tetrakis(4-carboxyphenylpyrazine), has been shown to be extremely successful in forming 17 metal–organic frameworks (MOFs). It was designed by Jiang and coworkers (Jiang *et al.*, 2017) who produced the first MOF using this ligand, *viz.* *catena*-[(μ -4,4',4'',4'''-pyrazine-2,3,5,6-tetrabenzoato)bis(*N,N*-dimethylformamide)dizinc unknown solvate] (NAWXER; Jiang *et al.*, 2017). Since then the ligand has been used by a number of groups, and the most recent MOF to be published is *catena*-[(μ -4,4'-bipyridine)bis(μ -hydroxo)bis[μ -dihydrogen 4,4',4'',4'''-(pyrazine-2,3,5,6-tetrayl)tetrabenzoato]trinickel unknown solvate] (HOQTUF; Wang *et al.*, 2019).

In relation to the structure of compound (III), a search for the substructure pyrrolo[3,4-*b*]pyrazine yielded only two hits. They concern dipyrrolo[3,4-*b*:3',4'-*e*]pyrazine structures that possess inversion symmetry, *viz.* 2,6-dibenzyl-1,2,3,5,6,7-hexahydrodipyrrolo[3,4-*b*:3',4'-*e*]pyrazine (EXUHIO; Gasser & Stoeckli-Evans, 2004) and 2,6-bis(4-methoxybenzyl)-1,2,3,5,6,7-hexahydrodipyrrolo[3,4-*b*:3',4'-*e*]pyrazine (EXUHOU; Gasser & Stoeckli-Evans, 2004). They were prepared during attempts to form 1,2,3,5,6,7-hexahydro-2,4,6,8-tetraaza-*s*-indacene by reacting 2,3,5,6-tetrakis(bromomethyl)pyrazine (Ferigo *et al.*, 1994; TOJXUN; Assoumatine & Stoeckli-Evans, 2014) with the corresponding amines. In contrast to (III), where the pyrrolo ring is planar (r.m.s. deviation = 0.029 Å) and inclined by only 2.00 (12)° to the pyrazine ring, here the pyrrolo groups have envelope conformations with the pyrrolo N atoms as the flaps. Their mean planes are inclined to the pyrazine ring by 7.88 (16)° in EXUHIO and by 8.05 (7)° in EXUHOU.

6. Synthesis and crystallization

Synthesis of 1,1',1'',1'''-(pyrazine-2,3,5,6-tetrayl) tetrakis(*N,N*-dimethylmethanamine) (I):

A large excess of dimethyl amine hydrochloride in water was neutralized with NaOH in an ice bath. Me₂NH formed *in situ* as a gas and was directly condensed in a round-bottom flask in an acetone/liquid N₂ bath at about 213 K using a weak vacuum. Once a sufficient quantity of liquid amine had formed, a solution of 2,3,5,6-tetrakis(bromomethyl)pyrazine (0.4530 g, 1 mmol) in 50 ml of CH₂Cl₂ was added dropwise at low temperature (*ca* 243 K). The reaction was left for about 4 h, allowing the temperature rise to RT. The excess amine was allowed to evaporate off before the solvent was gassed off. The residue obtained was dissolved in 40 ml of MeOH and

passed through a resin column (15 g of Dowex 1 X8) previously charged with OH[−] ions in order to exchange the HBr molecules, still attached to the ligand, by H₂O molecules. About 150 ml were used as eluent. Solvent evaporation yielded 0.27 g (87%) of a light-yellow powder of compound (I). Colourless block-like crystals were obtained by slow diffusion of hexane into a solution of the ligand in dichloromethane.

¹H NMR (CDCl₃, 200 MHz, ppm): 3.65 (*s*, 8H, CH₂), 2.15 (*s*, 12H, CH₃). ¹³C NMR (D₂O, 400 MHz, ppm): 152.16, 62.53, 46.54. IR (KBr pellet, cm^{−1}): 2974 (*s*), 2942 (*s*), 2854 (*m*), 2820 (*vs*), 2772 (*vs*), 1635 (*b*), 1456 (*s*), 1414 (*m*), 1348 (*s*), 1259 (*s*), 1204 (*m*), 1168 (*m*), 1027 (*vs*), 987 (*m*), 841 (*s*). MS (EI, 70 eV), *m/z*: 310 (MH⁺), 264, 178. Anal. for C₁₆H₃₂N₆ (308.5 g mol^{−1}) Calculated (%) C 62.30, H 10.46, N 27.24. Found (%) C 61.86, H 10.73, N 27.50.

Synthesis of *N,N',N'',N'''*-[pyrazine-2,3,5,6-tetrayltetrakis(methylene)]tetrakis(*N*-methylaniline) (II):

A solution of 2,3,5,6-tetrakis(bromomethyl)pyrazine (0.4530 g, 1 mmol) in 35 ml of CH₃CN was added dropwise to a suspension of *N*-methylaniline (1.2 ml, 10 mmol) and Na₂CO₃ (5.3 g, 50 mmol) in 25 ml of CH₃CN. The colour changed immediately from light to deep yellow. The mixture was refluxed for *ca* 2 h, followed by TLC and then cooled to RT. The white precipitate (NaBr and excess Na₂CO₃) was filtered off and the filtrate was evaporated under vacuum. The residue was dissolved in hexane and the insoluble yellow powder obtained was recovered, washed with more hexane and then dried to yield 0.335 g (60%) of compound (II). Pale-greenish-yellow block-like crystals were obtained by slow evaporation of a CDCl₃ solution of (II) in an NMR tube.

¹H NMR (CDCl₃, 200 MHz, ppm): 7.14 (*t*, 8H, ph), 6.68 (*m*, 12H, ph), 4.58 (*s*, 8H, CH₂), 2.79 (*s*, 12H, CH₃). ¹³C NMR (CD₃OD, 400 MHz, ppm): 149.64, 149.31, 128.94, 116.92, 113.17, 54.75, 39.46. IR (KBr pellet, cm^{−1}): 2926 (*w*), 1601 (*s*), 1508 (*vs*), 1446 (*m*), 1377 (*m*), 1366 (*m*), 1313 (*m*), 1257 (*m*), 1212 (*m*), 1117 (*w*), 993 (*w*), 820 (*w*), 745 (*s*), 689 (*m*). MS (EI, 70 eV), *m/z*: 594 (MK⁺), 374, 291. Analysis for C₃₆H₄₀N₆ (556.7 g mol^{−1}) Calculated (%) C 77.66, H 7.24, N 15.09. Found (%) C 76.82, H 7.19, N 15.07.

Synthesis of *N,N'*-[(6-phenyl-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyrazine-2,3-diyl)bis(methylene)]bis(*N*-methylaniline) (III):

Hexagonal pale-yellow plate-like crystals of compound (III) were obtained several times when reacting (II) with different metal salts, such as Zn(ClO₄)₂ (in excess), MnCl₂·4H₂O and Ni(AcO)₂·4H₂O. No spectroscopic or other analytical data are available for this compound.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The C-bound H atoms were included in calculated positions and treated as riding on their parent C atom: C–H = 0.93–0.97 Å with *U*_{iso}(H) = 1.5*U*_{eq}(C-methyl) and 1.2*U*_{eq}(C) for other H atoms. Note for compound (III): using the Stoe IPDS I, a one-circle diffractometer, to

Table 4
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	C ₁₆ H ₃₂ N ₆	C ₃₆ H ₄₀ N ₆	C ₂₈ H ₂₉ N ₅
<i>M_r</i>	308.47	556.74	435.56
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	293	293	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.7577 (14), 10.348 (2), 9.9118 (16)	8.6753 (10), 8.9160 (11), 10.0631 (10)	8.686 (1), 9.7731 (11), 14.3948 (16)
α , β , γ (°)	90, 101.663 (15), 90	85.774 (10), 73.468 (11), 82.467 (11)	85.915 (13), 75.349 (13), 78.891 (13)
<i>V</i> (Å ³)	980.2 (3)	739.21 (15)	1159.8 (2)
<i>Z</i>	2	1	2
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.07	0.08	0.08
Crystal size (mm)	0.53 × 0.53 × 0.26	0.38 × 0.30 × 0.27	0.45 × 0.35 × 0.10
Data collection			
Diffractometer	Stoe–Siemens AED2, 4-circle	Stoe–Siemens AED2, 4-circle	Stoe <i>IPDS</i> 1
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	3347, 1818, 1111	5354, 2741, 1913	8653, 3953, 1518
<i>R</i> _{int}	0.055	0.031	0.051
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.605	0.605	0.600
Refinement			
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.060, 0.154, 1.10	0.049, 0.108, 1.12	0.035, 0.079, 0.68
No. of reflections	1818	2741	3953
No. of parameters	105	193	301
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.15, -0.12	0.13, -0.15	0.12, -0.12

Computer programs: *STADIA* (Stoe & Cie, 1997), *EXPOSE*, *CELL* and *INTEGRATE* in *IPDS-I* (Stoe & Cie, 2004), *X-RED* (Stoe & Cie, 1997), *SHELXS97* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2020), *SHELXL2018/3* (Sheldrick, 2015), *PLATON* (Spek, 2020) and *pubCIF* (Westrip, 2010).

measure data for the triclinic system often only 93% of the Ewald sphere is accessible. Hence, the `diffn_reflns_Laue_measured_fraction_full` of 0.939 is below the required minimum of 0.95.

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supporting information

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Crystal structures and Hirshfeld surface analyses of two new tetrakis-substituted pyrazines and a degradation product

Ana Tesouro Vallina and Helen Stoeckli-Evans

Computing details

Data collection: *STADIA* (Stoe & Cie, 1997) for (I), (II); *EXPOSE* in *IPDS-I* (Stoe & Cie, 2004) for (III). Cell refinement: *STADIA* (Stoe & Cie, 1997) for (I), (II); *CELL* in *IPDS-I* (Stoe & Cie, 2004) for (III). Data reduction: *X-RED* (Stoe & Cie, 1997) for (I), (II); *INTEGRATE* in *IPDS-I* (Stoe & Cie, 2004) for (III). For all structures, program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *SHELXL2018/3* (Sheldrick, 2015), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

1,1',1'',1'''-(Pyrazine-2,3,5,6-tetrayl)tetrakis(*N,N*-dimethylmethanamine) (I)

Crystal data

$C_{16}H_{32}N_6$

$M_r = 308.47$

Monoclinic, $P2_1/n$

$a = 9.7577$ (14) Å

$b = 10.348$ (2) Å

$c = 9.9118$ (16) Å

$\beta = 101.663$ (15)°

$V = 980.2$ (3) Å³

$Z = 2$

$F(000) = 340$

$D_x = 1.045$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 22 reflections

$\theta = 12.6$ – 18.1 °

$\mu = 0.07$ mm⁻¹

$T = 293$ K

Block, colourless

$0.53 \times 0.53 \times 0.26$ mm

Data collection

Stoe–Siemens AED2, 4-circle diffractometer

Radiation source: fine-focus sealed tube

Plane graphite monochromator

$\omega/2\theta$ scans

3347 measured reflections

1818 independent reflections

1111 reflections with $I > 2\sigma(I)$

$R_{int} = 0.055$

$\theta_{max} = 25.5$ °, $\theta_{min} = 2.7$ °

$h = -11 \rightarrow 11$

$k = 0 \rightarrow 12$

$l = -11 \rightarrow 11$

2 standard reflections every 60 min

intensity decay: 1%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.060$

$wR(F^2) = 0.154$

$S = 1.10$

1818 reflections

105 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
 $w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 0.2847P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.15 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -0.12 \text{ e } \text{Å}^{-3}$
 Extinction correction: (SHELXL2018/3;
 Sheldrick, 2015),
 $F_c^* = kFc[1 + 0.001x\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.043 (7)

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 (Å^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.07379 (18)	0.10665 (19)	0.46684 (19)	0.0504 (5)
N2	0.2065 (2)	-0.0663 (2)	0.2414 (2)	0.0657 (7)
N3	0.1836 (2)	0.1754 (2)	0.8033 (2)	0.0699 (7)
C1	0.0393 (2)	0.0085 (2)	0.3779 (2)	0.0465 (6)
C2	0.0345 (2)	0.0981 (2)	0.5885 (2)	0.0476 (6)
C3	0.0864 (3)	0.0171 (3)	0.2426 (2)	0.0576 (7)
H3A	0.009971	-0.008061	0.168567	0.069*
H3B	0.111131	0.105746	0.226663	0.069*
C4	0.2207 (4)	-0.0957 (4)	0.1004 (3)	0.1046 (12)
H4A	0.234545	-0.016958	0.053752	0.157*
H4B	0.137243	-0.137698	0.052395	0.157*
H4C	0.299513	-0.151713	0.102710	0.157*
C5	0.3335 (3)	-0.0092 (4)	0.3188 (3)	0.0979 (12)
H5C	0.409862	-0.068297	0.321975	0.147*
H5B	0.322027	0.009064	0.410892	0.147*
H5A	0.352858	0.069624	0.275133	0.147*
C6	0.0739 (3)	0.2095 (2)	0.6863 (3)	0.0615 (7)
H6A	0.105348	0.281127	0.637289	0.074*
H6B	-0.008203	0.237656	0.719505	0.074*
C7	0.3174 (3)	0.1604 (4)	0.7623 (4)	0.1168 (15)
H7A	0.346508	0.242054	0.731787	0.175*
H7B	0.308288	0.098709	0.688686	0.175*
H7C	0.386012	0.130348	0.839465	0.175*
C8	0.1949 (4)	0.2720 (3)	0.9118 (3)	0.1000 (12)
H8A	0.107852	0.277166	0.942547	0.150*
H8B	0.215925	0.354560	0.876707	0.150*
H8C	0.268255	0.248005	0.987590	0.150*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0471 (11)	0.0513 (12)	0.0535 (12)	0.0003 (9)	0.0121 (9)	0.0005 (10)
N2	0.0654 (14)	0.0752 (16)	0.0629 (14)	0.0117 (12)	0.0279 (11)	0.0066 (12)
N3	0.0630 (14)	0.0758 (16)	0.0663 (14)	-0.0068 (12)	0.0021 (11)	-0.0189 (12)

C1	0.0433 (12)	0.0490 (14)	0.0465 (13)	0.0037 (11)	0.0076 (10)	0.0006 (12)
C2	0.0420 (12)	0.0478 (14)	0.0522 (14)	0.0030 (11)	0.0076 (10)	-0.0032 (11)
C3	0.0597 (15)	0.0629 (17)	0.0520 (14)	0.0059 (13)	0.0152 (12)	0.0041 (12)
C4	0.130 (3)	0.117 (3)	0.081 (2)	0.032 (2)	0.056 (2)	0.002 (2)
C5	0.0565 (17)	0.145 (3)	0.096 (2)	0.001 (2)	0.0259 (17)	0.019 (2)
C6	0.0660 (17)	0.0529 (15)	0.0666 (16)	-0.0012 (13)	0.0157 (13)	-0.0089 (13)
C7	0.060 (2)	0.154 (4)	0.131 (3)	-0.008 (2)	0.0089 (19)	-0.058 (3)
C8	0.105 (3)	0.111 (3)	0.078 (2)	-0.022 (2)	0.0064 (19)	-0.037 (2)

Geometric parameters (Å, °)

N1—C2	1.340 (3)	C4—H4B	0.9600
N1—C1	1.342 (3)	C4—H4C	0.9600
N2—C5	1.446 (4)	C5—H5C	0.9600
N2—C3	1.457 (3)	C5—H5B	0.9600
N2—C4	1.463 (3)	C5—H5A	0.9600
N3—C7	1.452 (4)	C6—H6A	0.9700
N3—C6	1.454 (3)	C6—H6B	0.9700
N3—C8	1.456 (3)	C7—H7A	0.9600
C1—C2 ⁱ	1.394 (3)	C7—H7B	0.9600
C1—C3	1.506 (3)	C7—H7C	0.9600
C2—C6	1.505 (3)	C8—H8A	0.9600
C3—H3A	0.9700	C8—H8B	0.9600
C3—H3B	0.9700	C8—H8C	0.9600
C4—H4A	0.9600		
C2—N1—C1	117.5 (2)	N2—C5—H5C	109.5
C5—N2—C3	111.0 (2)	N2—C5—H5B	109.5
C5—N2—C4	110.8 (2)	H5C—C5—H5B	109.5
C3—N2—C4	111.3 (2)	N2—C5—H5A	109.5
C7—N3—C6	111.2 (2)	H5C—C5—H5A	109.5
C7—N3—C8	110.0 (2)	H5B—C5—H5A	109.5
C6—N3—C8	110.9 (2)	N3—C6—C2	112.3 (2)
N1—C1—C2 ⁱ	121.0 (2)	N3—C6—H6A	109.1
N1—C1—C3	117.3 (2)	C2—C6—H6A	109.1
C2 ⁱ —C1—C3	121.7 (2)	N3—C6—H6B	109.1
N1—C2—C1 ⁱ	121.5 (2)	C2—C6—H6B	109.1
N1—C2—C6	116.5 (2)	H6A—C6—H6B	107.9
C1 ⁱ —C2—C6	121.9 (2)	N3—C7—H7A	109.5
N2—C3—C1	111.3 (2)	N3—C7—H7B	109.5
N2—C3—H3A	109.4	H7A—C7—H7B	109.5
C1—C3—H3A	109.4	N3—C7—H7C	109.5
N2—C3—H3B	109.4	H7A—C7—H7C	109.5
C1—C3—H3B	109.4	H7B—C7—H7C	109.5
H3A—C3—H3B	108.0	N3—C8—H8A	109.5
N2—C4—H4A	109.5	N3—C8—H8B	109.5
N2—C4—H4B	109.5	H8A—C8—H8B	109.5
H4A—C4—H4B	109.5	N3—C8—H8C	109.5

N2—C4—H4C	109.5	H8A—C8—H8C	109.5
H4A—C4—H4C	109.5	H8B—C8—H8C	109.5
H4B—C4—H4C	109.5		
C2—N1—C1—C2 ⁱ	-0.1 (3)	N1—C1—C3—N2	103.4 (2)
C2—N1—C1—C3	-178.68 (19)	C2 ⁱ —C1—C3—N2	-75.2 (3)
C1—N1—C2—C1 ⁱ	0.1 (3)	C7—N3—C6—C2	71.6 (3)
C1—N1—C2—C6	-179.79 (19)	C8—N3—C6—C2	-165.7 (2)
C5—N2—C3—C1	-77.0 (3)	N1—C2—C6—N3	-108.7 (2)
C4—N2—C3—C1	159.1 (2)	C1 ⁱ —C2—C6—N3	71.4 (3)

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3A \cdots N3 ⁱ	0.97	2.62	3.261 (4)	124

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

N,N',N'',N''' -[Pyrazine-2,3,5,6-tetrayltetrakis(methylene)]tetrakis(*N*-methylaniline) (II)

Crystal data

$C_{36}H_{40}N_6$
 $M_r = 556.74$
 Triclinic, $P\bar{1}$
 $a = 8.6753$ (10) \AA
 $b = 8.9160$ (11) \AA
 $c = 10.0631$ (10) \AA
 $\alpha = 85.774$ (10) $^\circ$
 $\beta = 73.468$ (11) $^\circ$
 $\gamma = 82.467$ (11) $^\circ$
 $V = 739.21$ (15) \AA^3

$Z = 1$
 $F(000) = 298$
 $D_x = 1.251$ Mg m^{-3}
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA
 Cell parameters from 28 reflections
 $\theta = 12.5\text{--}17.6^\circ$
 $\mu = 0.08$ mm^{-1}
 $T = 293$ K
 Block, pale-greenish-yellow
 $0.38 \times 0.30 \times 0.27$ mm

Data collection

Stoe–Siemens AED2, 4-circle diffractometer
 Radiation source: fine-focus sealed tube
 Plane graphite monochromator
 $\omega/2\theta$ scans
 5354 measured reflections
 2741 independent reflections
 1913 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$
 $\theta_{\text{max}} = 25.5^\circ$, $\theta_{\text{min}} = 2.1^\circ$
 $h = -9 \rightarrow 10$
 $k = -10 \rightarrow 10$
 $l = -12 \rightarrow 12$
 2 standard reflections every 60 min
 intensity decay: 1%

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.108$
 $S = 1.12$
 2741 reflections
 193 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
 $w = 1/[\sigma^2(F_o^2) + (0.0254P)^2 + 0.254P]$
 where $P = (F_o^2 + 2F_c^2)/3$

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

$$\Delta\rho_{\max} = 0.13 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.14 \text{ e } \text{\AA}^{-3}$$

Extinction correction: (SHELXL2018/3;
Sheldrick 2015),
 $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.026 (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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.46201 (19)	0.59971 (18)	0.89913 (16)	0.0393 (4)
N2	0.5739 (2)	0.31235 (19)	0.66461 (17)	0.0454 (4)
N3	0.2493 (2)	0.85914 (19)	0.95305 (17)	0.0481 (5)
C1	0.5585 (2)	0.4702 (2)	0.86471 (19)	0.0366 (5)
C2	0.4027 (2)	0.6301 (2)	1.0334 (2)	0.0378 (5)
C3	0.6246 (2)	0.4442 (2)	0.7110 (2)	0.0437 (5)
H3A	0.590818	0.533444	0.660508	0.052*
H3B	0.741879	0.433034	0.687257	0.052*
C4	0.4248 (3)	0.3268 (2)	0.63526 (19)	0.0429 (5)
C5	0.3070 (3)	0.4493 (3)	0.6795 (2)	0.0502 (6)
H5	0.328637	0.524582	0.728604	0.060*
C6	0.1604 (3)	0.4603 (3)	0.6515 (2)	0.0619 (7)
H6	0.083983	0.542794	0.682224	0.074*
C7	0.1237 (3)	0.3508 (3)	0.5785 (3)	0.0674 (7)
H7	0.024139	0.359185	0.559288	0.081*
C8	0.2367 (3)	0.2306 (3)	0.5354 (3)	0.0661 (7)
H8	0.212966	0.155880	0.486985	0.079*
C9	0.3863 (3)	0.2167 (2)	0.5618 (2)	0.0549 (6)
H9	0.461601	0.133665	0.530481	0.066*
C10	0.7008 (3)	0.2013 (3)	0.5894 (3)	0.0645 (7)
H10A	0.799406	0.208832	0.612583	0.097*
H10B	0.717471	0.220396	0.491434	0.097*
H10C	0.669345	0.101522	0.614401	0.097*
C11	0.2938 (3)	0.7782 (2)	1.0686 (2)	0.0488 (6)
H11A	0.195686	0.756971	1.138934	0.059*
H11B	0.348395	0.843600	1.108603	0.059*
C12	0.1177 (2)	0.8292 (2)	0.9122 (2)	0.0431 (5)
C13	0.0121 (3)	0.7258 (3)	0.9845 (2)	0.0586 (6)
H13	0.032849	0.671020	1.061037	0.070*
C14	-0.1220 (3)	0.7040 (3)	0.9440 (3)	0.0697 (7)
H14	-0.191144	0.635993	0.994996	0.084*
C15	-0.1562 (3)	0.7802 (3)	0.8302 (3)	0.0690 (7)
H15	-0.247073	0.765006	0.803564	0.083*
C16	-0.0517 (3)	0.8795 (3)	0.7571 (3)	0.0643 (7)
H16	-0.072129	0.931190	0.679059	0.077*

C17	0.0822 (3)	0.9052 (2)	0.7956 (2)	0.0516 (6)
H17	0.149960	0.973716	0.743706	0.062*
C18	0.3667 (3)	0.9499 (3)	0.8637 (3)	0.0633 (7)
H18A	0.407036	0.906772	0.774033	0.095*
H18B	0.454775	0.952213	0.903352	0.095*
H18C	0.316286	1.051147	0.854497	0.095*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0443 (10)	0.0408 (10)	0.0350 (9)	-0.0041 (8)	-0.0144 (7)	-0.0032 (7)
N2	0.0498 (11)	0.0481 (10)	0.0390 (10)	0.0057 (8)	-0.0163 (8)	-0.0112 (8)
N3	0.0541 (11)	0.0469 (11)	0.0455 (10)	0.0000 (9)	-0.0210 (9)	0.0016 (8)
C1	0.0371 (11)	0.0405 (11)	0.0347 (11)	-0.0066 (9)	-0.0126 (9)	-0.0044 (9)
C2	0.0400 (11)	0.0397 (11)	0.0366 (11)	-0.0044 (9)	-0.0147 (9)	-0.0040 (9)
C3	0.0454 (12)	0.0489 (12)	0.0360 (11)	-0.0029 (10)	-0.0106 (9)	-0.0039 (9)
C4	0.0523 (13)	0.0451 (12)	0.0314 (11)	-0.0027 (10)	-0.0142 (9)	0.0021 (9)
C5	0.0551 (14)	0.0576 (14)	0.0379 (12)	0.0042 (11)	-0.0159 (10)	-0.0098 (10)
C6	0.0490 (14)	0.0793 (18)	0.0521 (14)	0.0084 (13)	-0.0120 (11)	-0.0046 (13)
C7	0.0535 (15)	0.090 (2)	0.0637 (16)	-0.0169 (14)	-0.0239 (13)	0.0119 (15)
C8	0.0831 (19)	0.0582 (16)	0.0719 (17)	-0.0206 (14)	-0.0412 (15)	0.0038 (13)
C9	0.0747 (16)	0.0424 (13)	0.0524 (14)	-0.0010 (11)	-0.0275 (12)	-0.0030 (10)
C10	0.0631 (16)	0.0667 (16)	0.0613 (15)	0.0207 (13)	-0.0210 (12)	-0.0223 (13)
C11	0.0574 (14)	0.0506 (13)	0.0406 (12)	0.0052 (10)	-0.0210 (10)	-0.0074 (10)
C12	0.0464 (12)	0.0381 (11)	0.0429 (12)	0.0086 (9)	-0.0140 (10)	-0.0078 (9)
C13	0.0673 (16)	0.0563 (15)	0.0519 (14)	-0.0083 (12)	-0.0173 (12)	0.0048 (11)
C14	0.0597 (16)	0.0732 (18)	0.0723 (18)	-0.0179 (13)	-0.0071 (14)	-0.0057 (14)
C15	0.0550 (15)	0.0744 (18)	0.083 (2)	0.0020 (14)	-0.0280 (14)	-0.0203 (15)
C16	0.0704 (17)	0.0633 (16)	0.0654 (16)	0.0085 (13)	-0.0356 (14)	-0.0040 (13)
C17	0.0555 (14)	0.0492 (13)	0.0509 (13)	-0.0012 (11)	-0.0196 (11)	0.0026 (10)
C18	0.0677 (16)	0.0617 (15)	0.0676 (16)	-0.0143 (13)	-0.0287 (13)	0.0036 (13)

Geometric parameters (Å, °)

N1—C2	1.336 (2)	C8—H8	0.9300
N1—C1	1.339 (2)	C9—H9	0.9300
N2—C4	1.395 (3)	C10—H10A	0.9600
N2—C10	1.454 (3)	C10—H10B	0.9600
N2—C3	1.459 (3)	C10—H10C	0.9600
N3—C12	1.382 (3)	C11—H11A	0.9700
N3—C11	1.442 (2)	C11—H11B	0.9700
N3—C18	1.445 (3)	C12—C13	1.400 (3)
C1—C2 ⁱ	1.395 (3)	C12—C17	1.401 (3)
C1—C3	1.512 (3)	C13—C14	1.378 (3)
C2—C11	1.521 (3)	C13—H13	0.9300
C3—H3A	0.9700	C14—C15	1.374 (4)
C3—H3B	0.9700	C14—H14	0.9300
C4—C9	1.398 (3)	C15—C16	1.371 (4)

C4—C5	1.398 (3)	C15—H15	0.9300
C5—C6	1.369 (3)	C16—C17	1.375 (3)
C5—H5	0.9300	C16—H16	0.9300
C6—C7	1.384 (3)	C17—H17	0.9300
C6—H6	0.9300	C18—H18A	0.9600
C7—C8	1.359 (4)	C18—H18B	0.9600
C7—H7	0.9300	C18—H18C	0.9600
C8—C9	1.386 (3)		
C2—N1—C1	118.46 (16)	C7—C8—C9	121.7 (2)
C4—N2—C10	117.64 (17)	C7—C8—H8	119.2
C4—N2—C3	118.71 (16)	C9—C8—H8	119.2
C10—N2—C3	117.17 (18)	C8—C9—C4	120.4 (2)
C12—N3—C11	122.00 (18)	C8—C9—H9	119.8
C12—N3—C18	120.07 (17)	C4—C9—H9	119.8
C11—N3—C18	116.70 (18)	N3—C12—C13	122.77 (19)
N1—C1—C2 ⁱ	120.79 (16)	N3—C12—C17	120.5 (2)
N1—C1—C3	115.85 (16)	C13—C12—C17	116.7 (2)
C2 ⁱ —C1—C3	123.33 (17)	C14—C13—C12	121.0 (2)
N1—C2—C1 ⁱ	120.74 (17)	C14—C13—H13	119.5
N1—C2—C11	117.03 (17)	C12—C13—H13	119.5
C1 ⁱ —C2—C11	122.23 (17)	C15—C14—C13	121.6 (2)
N2—C3—C1	114.84 (17)	C15—C14—H14	119.2
N2—C3—H3A	108.6	C13—C14—H14	119.2
C1—C3—H3A	108.6	C16—C15—C14	117.7 (2)
N2—C3—H3B	108.6	C16—C15—H15	121.1
C1—C3—H3B	108.6	C14—C15—H15	121.1
H3A—C3—H3B	107.5	C15—C16—C17	122.1 (2)
N3—C11—C2	115.02 (17)	C15—C16—H16	119.0
N3—C11—H11A	108.5	C17—C16—H16	119.0
C2—C11—H11A	108.5	C16—C17—C12	120.8 (2)
N3—C11—H11B	108.5	C16—C17—H17	119.6
C2—C11—H11B	108.5	C12—C17—H17	119.6
H11A—C11—H11B	107.5	N3—C18—H18A	109.5
N2—C4—C9	120.81 (19)	N3—C18—H18B	109.5
N2—C4—C5	121.91 (19)	H18A—C18—H18B	109.5
C9—C4—C5	117.3 (2)	N3—C18—H18C	109.5
C6—C5—C4	121.1 (2)	H18A—C18—H18C	109.5
C6—C5—H5	119.5	H18B—C18—H18C	109.5
C4—C5—H5	119.5	N2—C10—H10A	109.5
C5—C6—C7	121.2 (2)	N2—C10—H10B	109.5
C5—C6—H6	119.4	H10A—C10—H10B	109.5
C7—C6—H6	119.4	N2—C10—H10C	109.5
C8—C7—C6	118.4 (2)	H10A—C10—H10C	109.5
C8—C7—H7	120.8	H10B—C10—H10C	109.5
C6—C7—H7	120.8		
C2—N1—C1—C2 ⁱ	-0.5 (3)	C4—C5—C6—C7	-0.1 (4)

C2—N1—C1—C3	-178.66 (17)	C5—C6—C7—C8	0.4 (4)
C1—N1—C2—C1 ⁱ	0.5 (3)	C6—C7—C8—C9	-0.6 (4)
C1—N1—C2—C11	179.92 (17)	C7—C8—C9—C4	0.5 (4)
C4—N2—C3—C1	83.8 (2)	N2—C4—C9—C8	178.8 (2)
C10—N2—C3—C1	-125.0 (2)	C5—C4—C9—C8	-0.2 (3)
N1—C1—C3—N2	-117.34 (19)	C11—N3—C12—C13	4.2 (3)
C2 ⁱ —C1—C3—N2	64.5 (2)	C18—N3—C12—C13	171.1 (2)
C12—N3—C11—C2	86.2 (2)	C11—N3—C12—C17	-177.13 (19)
C18—N3—C11—C2	-81.1 (2)	C18—N3—C12—C17	-10.2 (3)
N1—C2—C11—N3	8.2 (3)	N3—C12—C13—C14	177.1 (2)
C1 ⁱ —C2—C11—N3	-172.42 (18)	C17—C12—C13—C14	-1.7 (3)
C10—N2—C4—C9	14.5 (3)	C12—C13—C14—C15	1.2 (4)
C3—N2—C4—C9	165.50 (19)	C13—C14—C15—C16	0.1 (4)
C10—N2—C4—C5	-166.6 (2)	C14—C15—C16—C17	-0.8 (4)
C3—N2—C4—C5	-15.6 (3)	C15—C16—C17—C12	0.3 (4)
N2—C4—C5—C6	-178.9 (2)	N3—C12—C17—C16	-177.8 (2)
C9—C4—C5—C6	0.0 (3)	C13—C12—C17—C16	1.0 (3)

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

Hydrogen-bond geometry (\AA , $^\circ$)

$Cg2$ and $Cg3$ are the centroids of rings C4–C9 and C12–C17, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C5—H5 \cdots N1	0.93	2.50	3.331 (3)	149
C6—H6 \cdots $Cg3$	0.93	2.99	3.804 (3)	147
C3—H3A \cdots $Cg2^{ii}$	0.97	2.83	3.561 (2)	133

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

N,N' -[(6-Phenyl-6,7-dihydro-5H-pyrrolo[3,4- b]pyrazine-2,3-diyl)bis(methylene)]bis(N -methylaniline) (III)

Crystal data

$C_{28}H_{29}N_5$

$M_r = 435.56$

Triclinic, $P\bar{1}$

$a = 8.686$ (1) \AA

$b = 9.7731$ (11) \AA

$c = 14.3948$ (16) \AA

$\alpha = 85.915$ (13) $^\circ$

$\beta = 75.349$ (13) $^\circ$

$\gamma = 78.891$ (13) $^\circ$

$V = 1159.8$ (2) \AA^3

$Z = 2$

$F(000) = 464$

$D_x = 1.247$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA

Cell parameters from 5000 reflections

$\theta = 1.7\text{--}26.1^\circ$

$\mu = 0.08$ mm^{-1}

$T = 293$ K

Hexagonal plate, pale yellow

$0.45 \times 0.35 \times 0.10$ mm

Data collection

Stoe IPDS 1

diffractometer

Radiation source: fine-focus sealed tube

Plane graphite monochromator

φ rotation scans

8653 measured reflections

3953 independent reflections

1518 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.051$

$\theta_{\text{max}} = 25.3^\circ$, $\theta_{\text{min}} = 2.1^\circ$

$h = -10 \rightarrow 10$

$k = -11 \rightarrow 11$

$l = -17 \rightarrow 17$

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.035$ $wR(F^2) = 0.079$ $S = 0.68$

3953 reflections

301 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0308P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.12 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.12 \text{ e } \text{\AA}^{-3}$ Extinction correction: (SHELXL2018/3;
Sheldrick, 2015), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0154 (11)

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.4060 (2)	0.8786 (2)	0.20916 (11)	0.0559 (5)
N2	0.2666 (2)	0.9790 (2)	0.05437 (12)	0.0596 (6)
N3	0.5915 (2)	0.6863 (2)	-0.00687 (11)	0.0641 (6)
N4	-0.0765 (2)	1.1354 (2)	0.19845 (12)	0.0567 (5)
N5	0.2256 (2)	0.9508 (2)	0.39598 (12)	0.0607 (6)
C1	0.2797 (3)	0.9865 (2)	0.21849 (14)	0.0536 (6)
C2	0.4566 (2)	0.8223 (2)	0.12258 (14)	0.0510 (6)
C3	0.3862 (3)	0.8699 (3)	0.04787 (13)	0.0522 (6)
C4	0.2133 (2)	1.0385 (2)	0.14142 (15)	0.0550 (6)
C5	0.5911 (3)	0.7029 (2)	0.09341 (13)	0.0611 (7)
H5A	0.692953	0.724226	0.098842	0.073*
H5B	0.570113	0.619743	0.131738	0.073*
C6	0.4643 (2)	0.7825 (2)	-0.03875 (13)	0.0577 (7)
H6A	0.388274	0.733319	-0.055210	0.069*
H6B	0.508592	0.838726	-0.093682	0.069*
C7	0.6870 (3)	0.5773 (3)	-0.06142 (15)	0.0559 (6)
C8	0.8004 (3)	0.4812 (3)	-0.02614 (15)	0.0620 (7)
H8	0.810894	0.489435	0.035832	0.074*
C9	0.8976 (3)	0.3735 (3)	-0.08282 (17)	0.0725 (8)
H9	0.972506	0.309893	-0.058215	0.087*
C10	0.8853 (3)	0.3590 (3)	-0.17452 (19)	0.0773 (8)
H10	0.951563	0.286567	-0.212066	0.093*
C11	0.7738 (3)	0.4528 (3)	-0.21026 (16)	0.0764 (8)
H11	0.764776	0.443527	-0.272410	0.092*
C12	0.6751 (3)	0.5608 (3)	-0.15511 (15)	0.0665 (7)
H12	0.599899	0.623164	-0.180367	0.080*
C13	0.2210 (3)	1.0516 (2)	0.31746 (14)	0.0602 (7)

H13A	0.287658	1.119063	0.321236	0.072*
H13B	0.110758	1.101454	0.324780	0.072*
C14	0.1121 (3)	0.8654 (3)	0.42226 (14)	0.0560 (6)
C15	-0.0211 (3)	0.8838 (3)	0.38231 (15)	0.0629 (7)
H15	-0.032502	0.953551	0.335842	0.076*
C16	-0.1360 (3)	0.8000 (3)	0.41067 (19)	0.0781 (8)
H16	-0.224404	0.814656	0.383465	0.094*
C17	-0.1225 (4)	0.6956 (3)	0.4781 (2)	0.0906 (9)
H17	-0.199630	0.638472	0.496365	0.109*
C18	0.0080 (5)	0.6771 (3)	0.51850 (19)	0.0919 (10)
H18	0.017561	0.607346	0.565218	0.110*
C19	0.1240 (3)	0.7587 (3)	0.49158 (17)	0.0713 (8)
H19	0.211426	0.743206	0.519603	0.086*
C20	0.3718 (3)	0.9195 (3)	0.43102 (17)	0.0861 (9)
H20A	0.435685	0.990627	0.408568	0.129*
H20B	0.433210	0.830763	0.407665	0.129*
H20C	0.343173	0.916359	0.499973	0.129*
C21	0.0812 (3)	1.1664 (2)	0.14886 (15)	0.0651 (7)
H21A	0.106550	1.237790	0.183089	0.078*
H21B	0.077662	1.202914	0.084840	0.078*
C22	-0.1951 (3)	1.2457 (3)	0.24527 (14)	0.0534 (6)
C23	-0.1678 (3)	1.3796 (3)	0.24765 (15)	0.0688 (7)
H23	-0.069134	1.402028	0.213889	0.083*
C24	-0.2859 (4)	1.4813 (3)	0.29992 (19)	0.0860 (9)
H24	-0.264807	1.570861	0.301192	0.103*
C25	-0.4332 (4)	1.4517 (4)	0.34971 (19)	0.0920 (11)
H25	-0.511567	1.519698	0.385288	0.110*
C26	-0.4620 (3)	1.3199 (4)	0.34573 (18)	0.0911 (10)
H26	-0.562113	1.299000	0.378099	0.109*
C27	-0.3461 (3)	1.2173 (3)	0.29485 (16)	0.0719 (8)
H27	-0.368766	1.128393	0.293559	0.086*
C28	-0.1287 (3)	1.0303 (3)	0.15362 (17)	0.0805 (8)
H28A	-0.200292	0.983359	0.201593	0.121*
H28B	-0.036112	0.963950	0.123096	0.121*
H28C	-0.184352	1.073996	0.106462	0.121*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0524 (11)	0.0660 (15)	0.0465 (11)	-0.0088 (11)	-0.0077 (9)	-0.0042 (9)
N2	0.0533 (12)	0.0728 (15)	0.0465 (11)	-0.0058 (11)	-0.0064 (9)	0.0024 (10)
N3	0.0620 (12)	0.0785 (16)	0.0446 (11)	0.0103 (12)	-0.0146 (9)	-0.0111 (10)
N4	0.0522 (12)	0.0551 (14)	0.0605 (11)	-0.0069 (11)	-0.0106 (10)	-0.0064 (10)
N5	0.0562 (13)	0.0813 (17)	0.0459 (11)	-0.0163 (12)	-0.0104 (10)	-0.0081 (10)
C1	0.0503 (14)	0.0603 (18)	0.0468 (13)	-0.0137 (13)	-0.0020 (11)	-0.0047 (11)
C2	0.0461 (13)	0.0629 (17)	0.0413 (13)	-0.0085 (13)	-0.0070 (11)	-0.0013 (12)
C3	0.0469 (13)	0.0650 (17)	0.0419 (13)	-0.0106 (13)	-0.0056 (11)	0.0000 (12)
C4	0.0498 (14)	0.0601 (17)	0.0505 (14)	-0.0082 (13)	-0.0063 (12)	0.0022 (12)

C5	0.0567 (14)	0.0749 (19)	0.0467 (13)	-0.0009 (14)	-0.0100 (11)	-0.0089 (12)
C6	0.0524 (14)	0.0736 (18)	0.0449 (12)	-0.0084 (13)	-0.0094 (11)	-0.0039 (12)
C7	0.0486 (14)	0.0627 (18)	0.0532 (14)	-0.0095 (14)	-0.0052 (11)	-0.0076 (12)
C8	0.0555 (14)	0.0709 (19)	0.0563 (14)	-0.0066 (15)	-0.0098 (12)	-0.0068 (13)
C9	0.0645 (17)	0.069 (2)	0.0777 (18)	-0.0034 (15)	-0.0112 (14)	-0.0085 (15)
C10	0.0739 (19)	0.074 (2)	0.0766 (18)	-0.0108 (17)	0.0001 (15)	-0.0247 (15)
C11	0.0800 (19)	0.088 (2)	0.0597 (15)	-0.0135 (18)	-0.0103 (14)	-0.0186 (15)
C12	0.0623 (16)	0.080 (2)	0.0562 (15)	-0.0069 (15)	-0.0135 (12)	-0.0119 (13)
C13	0.0618 (16)	0.0653 (18)	0.0513 (13)	-0.0143 (13)	-0.0053 (11)	-0.0109 (13)
C14	0.0589 (16)	0.0647 (19)	0.0397 (13)	-0.0072 (15)	-0.0032 (12)	-0.0143 (12)
C15	0.0598 (16)	0.074 (2)	0.0540 (14)	-0.0175 (15)	-0.0057 (13)	-0.0109 (13)
C16	0.070 (2)	0.085 (2)	0.0761 (18)	-0.0172 (18)	-0.0039 (15)	-0.0237 (17)
C17	0.092 (2)	0.079 (3)	0.092 (2)	-0.039 (2)	0.0180 (18)	-0.0243 (19)
C18	0.127 (3)	0.069 (2)	0.0706 (19)	-0.018 (2)	-0.006 (2)	-0.0067 (15)
C19	0.086 (2)	0.064 (2)	0.0615 (16)	-0.0086 (17)	-0.0154 (14)	-0.0066 (14)
C20	0.0670 (17)	0.122 (3)	0.0789 (17)	-0.0167 (17)	-0.0316 (14)	-0.0145 (16)
C21	0.0603 (16)	0.0617 (19)	0.0639 (14)	-0.0040 (14)	-0.0043 (12)	0.0023 (13)
C22	0.0536 (16)	0.0608 (19)	0.0442 (12)	-0.0012 (14)	-0.0162 (11)	0.0003 (12)
C23	0.0726 (17)	0.061 (2)	0.0673 (16)	-0.0041 (17)	-0.0117 (13)	-0.0061 (14)
C24	0.100 (2)	0.065 (2)	0.0893 (19)	0.0040 (19)	-0.0269 (18)	-0.0202 (16)
C25	0.081 (2)	0.110 (3)	0.0742 (19)	0.019 (2)	-0.0162 (17)	-0.0368 (19)
C26	0.0629 (18)	0.121 (3)	0.0784 (19)	0.003 (2)	-0.0059 (14)	-0.0256 (19)
C27	0.0598 (16)	0.080 (2)	0.0711 (15)	-0.0083 (16)	-0.0100 (14)	-0.0066 (14)
C28	0.0687 (17)	0.086 (2)	0.0927 (18)	-0.0024 (16)	-0.0318 (15)	-0.0313 (16)

Geometric parameters (Å, °)

N1—C2	1.333 (2)	C12—H12	0.9300
N1—C1	1.354 (2)	C13—H13A	0.9700
N2—C3	1.328 (2)	C13—H13B	0.9700
N2—C4	1.352 (2)	C14—C15	1.394 (3)
N3—C7	1.374 (2)	C14—C19	1.398 (3)
N3—C6	1.453 (2)	C15—C16	1.376 (3)
N3—C5	1.463 (2)	C15—H15	0.9300
N4—C22	1.415 (3)	C16—C17	1.367 (4)
N4—C28	1.449 (3)	C16—H16	0.9300
N4—C21	1.453 (3)	C17—C18	1.376 (4)
N5—C14	1.376 (3)	C17—H17	0.9300
N5—C13	1.449 (3)	C18—C19	1.367 (4)
N5—C20	1.454 (3)	C18—H18	0.9300
C1—C4	1.397 (3)	C19—H19	0.9300
C1—C13	1.527 (3)	C20—H20A	0.9600
C2—C3	1.377 (2)	C20—H20B	0.9600
C2—C5	1.483 (3)	C20—H20C	0.9600
C3—C6	1.498 (3)	C21—H21A	0.9700
C4—C21	1.515 (3)	C21—H21B	0.9700
C5—H5A	0.9700	C22—C23	1.378 (3)
C5—H5B	0.9700	C22—C27	1.395 (3)

C6—H6A	0.9700	C23—C24	1.390 (3)
C6—H6B	0.9700	C23—H23	0.9300
C7—C8	1.392 (3)	C24—C25	1.373 (4)
C7—C12	1.401 (3)	C24—H24	0.9300
C8—C9	1.385 (3)	C25—C26	1.366 (4)
C8—H8	0.9300	C25—H25	0.9300
C9—C10	1.370 (3)	C26—C27	1.378 (3)
C9—H9	0.9300	C26—H26	0.9300
C10—C11	1.373 (3)	C27—H27	0.9300
C10—H10	0.9300	C28—H28A	0.9600
C11—C12	1.380 (3)	C28—H28B	0.9600
C11—H11	0.9300	C28—H28C	0.9600
C2—N1—C1	114.96 (16)	C1—C13—H13B	108.9
C3—N2—C4	115.23 (17)	H13A—C13—H13B	107.7
C7—N3—C6	122.57 (16)	N5—C14—C15	121.3 (2)
C7—N3—C5	123.11 (17)	N5—C14—C19	121.3 (2)
C6—N3—C5	113.64 (16)	C15—C14—C19	117.3 (3)
C22—N4—C28	118.35 (19)	C16—C15—C14	120.9 (3)
C22—N4—C21	117.9 (2)	C16—C15—H15	119.5
C28—N4—C21	114.48 (18)	C14—C15—H15	119.5
C14—N5—C13	120.75 (19)	C17—C16—C15	121.1 (3)
C14—N5—C20	119.8 (2)	C17—C16—H16	119.4
C13—N5—C20	117.9 (2)	C15—C16—H16	119.4
N1—C1—C4	122.07 (18)	C16—C17—C18	118.5 (3)
N1—C1—C13	115.34 (18)	C16—C17—H17	120.8
C4—C1—C13	122.5 (2)	C18—C17—H17	120.8
N1—C2—C3	122.80 (19)	C19—C18—C17	121.6 (3)
N1—C2—C5	125.96 (18)	C19—C18—H18	119.2
C3—C2—C5	111.24 (18)	C17—C18—H18	119.2
N2—C3—C2	123.17 (19)	C18—C19—C14	120.6 (3)
N2—C3—C6	126.31 (18)	C18—C19—H19	119.7
C2—C3—C6	110.52 (19)	C14—C19—H19	119.7
N2—C4—C1	121.65 (19)	N5—C20—H20A	109.5
N2—C4—C21	115.81 (19)	N5—C20—H20B	109.5
C1—C4—C21	122.52 (19)	H20A—C20—H20B	109.5
N3—C5—C2	102.26 (16)	N5—C20—H20C	109.5
N3—C5—H5A	111.3	H20A—C20—H20C	109.5
C2—C5—H5A	111.3	H20B—C20—H20C	109.5
N3—C5—H5B	111.3	N4—C21—C4	112.0 (2)
C2—C5—H5B	111.3	N4—C21—H21A	109.2
H5A—C5—H5B	109.2	C4—C21—H21A	109.2
N3—C6—C3	102.22 (16)	N4—C21—H21B	109.2
N3—C6—H6A	111.3	C4—C21—H21B	109.2
C3—C6—H6A	111.3	H21A—C21—H21B	107.9
N3—C6—H6B	111.3	C23—C22—C27	117.8 (2)
C3—C6—H6B	111.3	C23—C22—N4	123.5 (2)
H6A—C6—H6B	109.2	C27—C22—N4	118.7 (3)

N3—C7—C8	121.19 (19)	C22—C23—C24	120.7 (3)
N3—C7—C12	120.9 (2)	C22—C23—H23	119.6
C8—C7—C12	117.9 (2)	C24—C23—H23	119.6
C9—C8—C7	120.4 (2)	C25—C24—C23	121.0 (3)
C9—C8—H8	119.8	C25—C24—H24	119.5
C7—C8—H8	119.8	C23—C24—H24	119.5
C10—C9—C8	121.2 (2)	C26—C25—C24	118.4 (3)
C10—C9—H9	119.4	C26—C25—H25	120.8
C8—C9—H9	119.4	C24—C25—H25	120.8
C9—C10—C11	119.1 (2)	C25—C26—C27	121.5 (3)
C9—C10—H10	120.4	C25—C26—H26	119.3
C11—C10—H10	120.4	C27—C26—H26	119.3
C10—C11—C12	120.8 (2)	C26—C27—C22	120.6 (3)
C10—C11—H11	119.6	C26—C27—H27	119.7
C12—C11—H11	119.6	C22—C27—H27	119.7
C11—C12—C7	120.6 (2)	N4—C28—H28A	109.5
C11—C12—H12	119.7	N4—C28—H28B	109.5
C7—C12—H12	119.7	H28A—C28—H28B	109.5
N5—C13—C1	113.53 (19)	N4—C28—H28C	109.5
N5—C13—H13A	108.9	H28A—C28—H28C	109.5
C1—C13—H13A	108.9	H28B—C28—H28C	109.5
N5—C13—H13B	108.9		
C2—N1—C1—C4	-2.9 (3)	N3—C7—C12—C11	178.6 (2)
C2—N1—C1—C13	-180.0 (2)	C8—C7—C12—C11	-0.4 (3)
C1—N1—C2—C3	0.0 (3)	C14—N5—C13—C1	-75.0 (2)
C1—N1—C2—C5	-179.5 (2)	C20—N5—C13—C1	91.0 (3)
C4—N2—C3—C2	-2.3 (3)	N1—C1—C13—N5	-37.6 (3)
C4—N2—C3—C6	178.1 (2)	C4—C1—C13—N5	145.3 (2)
N1—C2—C3—N2	2.8 (3)	C13—N5—C14—C15	-7.6 (3)
C5—C2—C3—N2	-177.7 (2)	C20—N5—C14—C15	-173.29 (19)
N1—C2—C3—C6	-177.6 (2)	C13—N5—C14—C19	173.80 (19)
C5—C2—C3—C6	2.0 (3)	C20—N5—C14—C19	8.1 (3)
C3—N2—C4—C1	-0.6 (3)	N5—C14—C15—C16	-178.5 (2)
C3—N2—C4—C21	177.8 (2)	C19—C14—C15—C16	0.2 (3)
N1—C1—C4—N2	3.4 (3)	C14—C15—C16—C17	-0.6 (4)
C13—C1—C4—N2	-179.8 (2)	C15—C16—C17—C18	0.9 (4)
N1—C1—C4—C21	-174.9 (2)	C16—C17—C18—C19	-1.0 (4)
C13—C1—C4—C21	2.0 (3)	C17—C18—C19—C14	0.7 (4)
C7—N3—C5—C2	-173.1 (2)	N5—C14—C19—C18	178.4 (2)
C6—N3—C5—C2	-2.3 (2)	C15—C14—C19—C18	-0.3 (3)
N1—C2—C5—N3	179.7 (2)	C22—N4—C21—C4	154.45 (18)
C3—C2—C5—N3	0.1 (2)	C28—N4—C21—C4	-59.3 (2)
C7—N3—C6—C3	174.2 (2)	N2—C4—C21—N4	103.8 (2)
C5—N3—C6—C3	3.3 (2)	C1—C4—C21—N4	-77.8 (3)
N2—C3—C6—N3	176.5 (2)	C28—N4—C22—C23	-146.2 (2)
C2—C3—C6—N3	-3.2 (2)	C21—N4—C22—C23	-1.2 (3)
C6—N3—C7—C8	-175.5 (2)	C28—N4—C22—C27	36.3 (3)

C5—N3—C7—C8	−5.5 (3)	C21—N4—C22—C27	−178.72 (19)
C6—N3—C7—C12	5.6 (3)	C27—C22—C23—C24	1.6 (3)
C5—N3—C7—C12	175.6 (2)	N4—C22—C23—C24	−175.92 (19)
N3—C7—C8—C9	−178.8 (2)	C22—C23—C24—C25	−0.6 (4)
C12—C7—C8—C9	0.1 (3)	C23—C24—C25—C26	−0.8 (4)
C7—C8—C9—C10	0.2 (4)	C24—C25—C26—C27	1.3 (4)
C8—C9—C10—C11	−0.3 (4)	C25—C26—C27—C22	−0.3 (4)
C9—C10—C11—C12	0.1 (4)	C23—C22—C27—C26	−1.2 (3)
C10—C11—C12—C7	0.3 (4)	N4—C22—C27—C26	176.5 (2)

Hydrogen-bond geometry (Å, °)

*Cg*2 and *Cg*3 are the centroids of rings N1/N2/C1–C4 and C7–C12, respectively.

<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>
C15—H15...N4	0.93	2.61	3.542 (3)	175
C28—H28 <i>B</i> ...N2	0.96	2.59	3.323 (3)	133
C6—H6 <i>B</i> ... <i>Cg</i> 2 ⁱ	0.97	2.82	3.601 (2)	138
C23—H23... <i>Cg</i> 3 ⁱ	0.93	2.97	3.881 (3)	168

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