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Methyl 4-{*N*′-[(1*E*)-1-(pyrazin-2-yl)ethylidene]-hydrazinecarbonyl}benzoate

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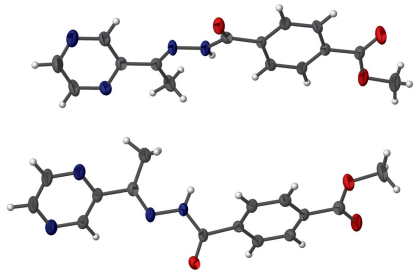
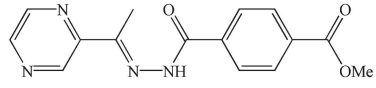
The title Schiff base, $C_{15}H_{14}N_4O_3$, was synthesized by the condensation reaction between caprylic hydrazide and 2-acetylpyrazine. There are two independent pseudo-enantiomeric molecules, *A* and *B*, in the asymmetric unit that differ mainly in the orientation of the hydrazone units. For example, the dihedral angles between the benzene and pyrazine rings are 20.836 (13) (*A*) and 15.701 (14)° (*B*). The molecular packing features N—H···O hydrogen bonds that lead to a twisted supramolecular chain along the *b*-axis direction. The presence of C—H···O interactions consolidates the chains into a three-dimensional architecture. The studied sample was a two-component twin.

3D view



Chemical scheme



Structure description

Hydrazone-based Schiff bases are important members of the Schiff base family. Their method of synthesis is simple and products can be tailored by changing the aldehyde or ketone and caprylic hydrazide precursors. Their applications are focused upon molecular switches (Coskun *et al.*, 2012), sensors (Albelda *et al.*, 2012) and single molecule magnets (SMMs; Tian *et al.*, 2013) as a result of their ability to adopt variable coordination modes towards metals. 2-Acetylpyrazine-based hydrazone ligands and their transition metal chemistry have also been reported (Hou *et al.*, 2018; Li *et al.*, 2015). Herein, we aimed to synthesize a new hydrazone ligand substituted with 2-acetylpyrazine to enrich its potential coordination chemistry with transition metals; the successful synthesis of the hydrazone ligand was confirmed by its X-ray crystal structure determination.

The asymmetric unit of the title molecule, Fig. 1, comprises two independent molecules (*A* and *B*) that differ primarily in the relative orientation about the hydrazone bond. In molecule *A*, the benzene and pyrazine rings make a dihedral angle of 20.836 (13)°, the

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O6^{i}	0.86	2.31	3.063 (5)	147
N5—H5···O3^{ii}	0.86	2.39	3.172 (5)	151
C10—H10···O4^{iii}	0.93	2.51	3.440 (7)	175
C12—H12A···O3^{iv}	0.96	2.38	3.327 (6)	171
C12—H12C···O6^{i}	0.96	2.58	3.360 (6)	139
C28—H28A···O3^{ii}	0.96	2.59	3.422 (6)	145

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

corresponding angle in molecule *B* being 15.701 (14)°. In the crystal, N—H···O hydrogen bonds lead to twisted supramolecular chains along the *b*-axis direction, which are consolidated by C—H···O interactions, Table 1 and Fig. 2, leading to a three-dimensional architecture. Molecules *A* and *B* are also linked through π–π interactions between benzene rings with an offset centroid–centroid distance of 3.739 (3) Å, and pyrazine rings with an offset centroid–centroid distance of 4.0519 (3) Å.

Synthesis and crystallization

All reagents and solvents were purchased from commercial sources and used as received without further purification. The title molecule was synthesized *via* two steps; firstly, the intermediate caprylic hydrazide was prepared by refluxing dimethyl terephthalate (3.08 g,19.4 mmol) and an excess of hydrazine hydrate (2.94 g, 58.8 mmol) in methanol (40 ml). After 50 min., a white precipitate was evident, and after refluxing for an additional 15 h the suspension was cooled to room temperature. A white solid was filtered off and used in the next step. The title molecule was prepared by the condensation reaction of pyrazine-2-carbohydrazide (1.38 g, 10 mmol) with 2-acetylpyrazine (1.22 g,10 mmol) under reflux in ethanol (50 ml) for 16 h. A transparent, light-yellow solution resulted. Colourless crystals suitable for X-ray analysis precipitated overnight.

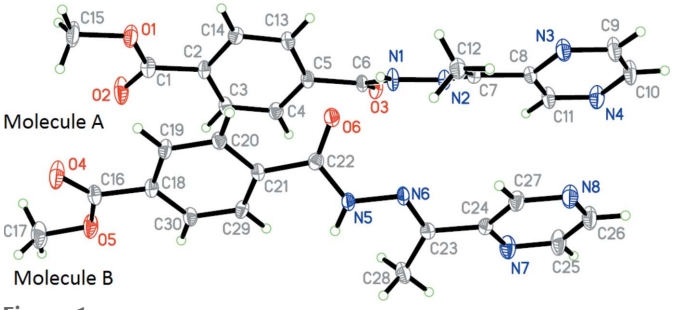


Figure 1
The molecular structure of the title compound showing the atom numbering and displacement ellipsoids drawn at the 50% probability level.

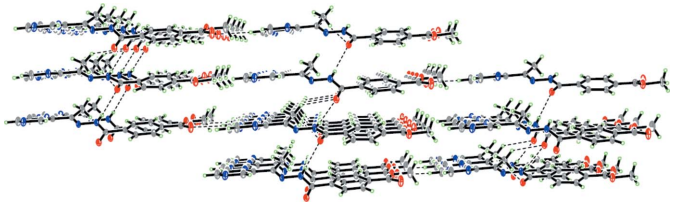


Figure 2
Molecular packing for the title compound viewed along the *b*-axis direction. Dashed lines indicate hydrogen bonding.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{15}H_{14}N_4O_3$
M_r	298.30
Crystal system, space group	Triclinic, $P1$
Temperature (K)	296
a, b, c (Å)	5.859 (5), 7.479 (6), 16.329 (14)
α, β, γ (°)	93.818 (12), 91.29 (3), 94.252 (10)
V (Å^3)	711.7 (10)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.2 × 0.14 × 0.12
Data collection	
Diffractometer	Bruker P4
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.654, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5678, 4773, 3720
R_{int}	0.026
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.651
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.050, 0.106, 1.12
No. of reflections	4773
No. of parameters	402
No. of restraints	3
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.19, −0.29
Absolute structure	Refined as an inversion twin.
Absolute structure parameter	−2 (2)

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The sample was refined as an inversion twin.

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References

Albelda, M. T., Frías, J. C., García-España, E. & Schneider, H. J. (2012). *Chem. Soc. Rev.* **41**, 3859–3877.
Bruker (2013). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2014). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Coskun, A., Banaszak, M., Astumian, R. D., Stoddart, J. F. & Grzybowski, B. A. (2012). *Chem. Soc. Rev.* **41**, 19–30.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Hou, X.-F., Zhao, X.-L., Zhang, L., Wu, W.-N. & Wang, Y. (2018). *Chin. J. Inorg. Chem.* **34**, 201–205.
Li, C.-R., Liao, Z.-C., Qin, J.-C., Wang, B.-D. & Yang, Z.-Y. (2015). *J. Lumin.* **168**, 330–333.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Tian, H.-Q., Zhao, L., Lin, H.-F., Tang, J.-K. & Li, G.-S. (2013). *Chem. Eur. J.* **19**, 13235–13241.

full crystallographic data

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Crystal data

$C_{15}H_{14}N_4O_3$
M_r = 298.30
Triclinic, $P\overline{1}$
a = 5.859 (5) Å
b = 7.479 (6) Å
c = 16.329 (14) Å
α = 93.818 (12)°
β = 91.29 (3)°
γ = 94.252 (10)°
V = 711.7 (10) Å^3
Z = 2
$F(000)$ = 312
D_x = 1.392 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1904 reflections
θ = 2.5–27.2°
μ = 0.10 mm^{-1}
T = 296 K
Block, colourless
0.2 × 0.14 × 0.12 mm

Data collection

Bruker P4 diffractometer
ω scan
Absorption correction: multi-scan (SADABS; Bruker, 2014)
T_{min} = 0.654, T_{max} = 0.746
5678 measured reflections
4773 independent reflections
3720 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 27.6°, θ_{min} = 2.5°
h = −7→7
k = −9→9
l = −21→21
1 standard reflections every 60 reflections
intensity decay: 1%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.106
S = 1.12
4773 reflections
402 parameters
3 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 0.0177P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}
Absolute structure: Refined as an inversion twin.
Absolute structure parameter: −2 (2)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a 2-component inversion twin. The carbon-bound H-atoms were placed in calculated positions (C—H = 0.93–0.96 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2–1.5U_{equiv}(C). The N-bound H atoms were fixed with a distance restraint of 0.86 Å, and with U_{iso}(H) = 1.2U_{eq}(N).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.3039 (5)	0.6312 (5)	0.84591 (19)	0.0456 (9)
O2	−0.0696 (6)	0.5807 (5)	0.8700 (2)	0.0603 (11)
O3	−0.2556 (5)	0.9093 (4)	0.48052 (17)	0.0385 (8)
N1	0.0715 (6)	0.7886 (5)	0.4389 (2)	0.0363 (9)
H1	0.184869	0.728662	0.452142	0.044*
N2	0.0480 (6)	0.8439 (5)	0.3598 (2)	0.0347 (9)
N3	0.3753 (6)	0.8849 (5)	0.1848 (2)	0.0426 (10)
N4	−0.0495 (6)	0.9510 (6)	0.1154 (2)	0.0473 (11)
C1	0.0809 (8)	0.6288 (6)	0.8255 (3)	0.0385 (12)
C2	0.0443 (7)	0.6855 (6)	0.7409 (3)	0.0289 (10)
C3	−0.1726 (7)	0.6523 (6)	0.7041 (3)	0.0345 (11)
H3	−0.291685	0.600059	0.733219	0.041*
C4	−0.2120 (7)	0.6966 (6)	0.6244 (3)	0.0317 (10)
H4	−0.357790	0.674991	0.600369	0.038*
C5	−0.0347 (7)	0.7733 (5)	0.5799 (3)	0.0280 (10)
C6	−0.0871 (7)	0.8304 (6)	0.4950 (3)	0.0289 (10)
C7	0.2074 (7)	0.8007 (6)	0.3105 (3)	0.0309 (10)
C8	0.1809 (7)	0.8627 (5)	0.2262 (2)	0.0304 (10)
C9	0.3527 (8)	0.9423 (7)	0.1097 (3)	0.0505 (14)
H9	0.483598	0.960426	0.079224	0.061*
C10	0.1469 (8)	0.9758 (7)	0.0753 (3)	0.0498 (14)
H10	0.142571	1.016919	0.022801	0.060*
C11	−0.0282 (7)	0.8952 (6)	0.1906 (3)	0.0394 (12)
H11	−0.159514	0.877206	0.220823	0.047*
C12	0.4108 (7)	0.7020 (6)	0.3303 (3)	0.0383 (11)
H12A	0.507850	0.773304	0.370007	0.057*
H12B	0.494175	0.678822	0.281220	0.057*
H12C	0.361537	0.590111	0.352291	0.057*
C13	0.1824 (7)	0.8081 (6)	0.6165 (3)	0.0326 (10)
H13	0.301552	0.859409	0.587081	0.039*
C14	0.2203 (7)	0.7662 (6)	0.6966 (3)	0.0322 (10)
H14	0.364645	0.792025	0.721296	0.039*
C15	0.3571 (8)	0.5638 (7)	0.9260 (3)	0.0579 (15)
H15A	0.295206	0.441498	0.927091	0.087*
H15B	0.290641	0.636338	0.968545	0.087*
H15C	0.520079	0.569500	0.934761	0.087*
O4	1.0985 (5)	0.1083 (5)	0.8783 (2)	0.0585 (11)
O5	0.7286 (5)	0.0840 (5)	0.83908 (19)	0.0499 (9)
O6	1.3020 (4)	0.4597 (4)	0.49293 (17)	0.0372 (7)
N5	0.9896 (6)	0.2855 (5)	0.4416 (2)	0.0319 (9)
H5	0.880665	0.207106	0.451585	0.038*

N6	1.0116 (6)	0.3429 (5)	0.3625 (2)	0.0326 (9)
N7	0.6591 (6)	0.3785 (6)	0.1892 (2)	0.0441 (10)
N8	1.0817 (6)	0.4420 (6)	0.1156 (2)	0.0468 (11)
C16	0.9514 (7)	0.1210 (6)	0.8273 (3)	0.0339 (11)
C17	0.6688 (9)	0.0272 (8)	0.9194 (3)	0.0625 (16)
H17A	0.505206	0.015827	0.923408	0.094*
H17B	0.732812	0.114865	0.960868	0.094*
H17C	0.728723	−0.086637	0.927206	0.094*
C18	0.9934 (7)	0.1775 (5)	0.7422 (3)	0.0296 (10)
C19	1.2130 (7)	0.2443 (6)	0.7237 (3)	0.0321 (11)
H19	1.330460	0.250763	0.763264	0.039*
C20	1.2559 (6)	0.3010 (5)	0.6461 (3)	0.0293 (10)
H20	1.401801	0.348178	0.634193	0.035*
C21	1.0823 (7)	0.2879 (5)	0.5858 (3)	0.0262 (9)
C22	1.1377 (7)	0.3515 (5)	0.5028 (3)	0.0285 (10)
C23	0.8349 (7)	0.3018 (5)	0.3149 (3)	0.0287 (10)
C24	0.8557 (7)	0.3584 (5)	0.2296 (3)	0.0297 (10)
C25	0.6773 (8)	0.4326 (7)	0.1131 (3)	0.0520 (15)
H25	0.544231	0.449099	0.083317	0.062*
C26	0.8838 (8)	0.4646 (7)	0.0771 (3)	0.0491 (14)
H26	0.886154	0.503283	0.024169	0.059*
C27	1.0638 (7)	0.3898 (6)	0.1920 (3)	0.0369 (11)
H27	1.197488	0.373669	0.221456	0.044*
C28	0.6158 (7)	0.2061 (7)	0.3387 (3)	0.0447 (12)
H28A	0.645604	0.089600	0.355952	0.067*
H28B	0.510368	0.192739	0.292468	0.067*
H28C	0.550842	0.274419	0.383007	0.067*
C29	0.8626 (7)	0.2227 (5)	0.6058 (3)	0.0301 (10)
H29	0.744564	0.215790	0.566363	0.036*
C30	0.8188 (7)	0.1685 (6)	0.6832 (3)	0.0316 (10)
H30	0.671581	0.125808	0.695868	0.038*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0410 (19)	0.068 (2)	0.029 (2)	0.0028 (16)	−0.0042 (14)	0.0172 (17)
O2	0.046 (2)	0.107 (3)	0.033 (2)	0.0108 (19)	0.0100 (16)	0.031 (2)
O3	0.0421 (17)	0.0496 (19)	0.0261 (18)	0.0162 (14)	−0.0021 (13)	0.0071 (15)
N1	0.042 (2)	0.050 (2)	0.020 (2)	0.0162 (18)	0.0068 (16)	0.0125 (18)
N2	0.042 (2)	0.043 (2)	0.020 (2)	0.0056 (17)	0.0027 (17)	0.0098 (18)
N3	0.035 (2)	0.065 (3)	0.029 (2)	0.0008 (18)	0.0042 (16)	0.013 (2)
N4	0.043 (2)	0.071 (3)	0.029 (2)	0.010 (2)	0.0032 (18)	0.012 (2)
C1	0.043 (3)	0.045 (3)	0.029 (3)	0.010 (2)	0.003 (2)	0.007 (2)
C2	0.035 (2)	0.034 (2)	0.019 (2)	0.0088 (19)	0.0041 (18)	0.0047 (19)
C3	0.032 (2)	0.045 (3)	0.029 (3)	0.009 (2)	0.009 (2)	0.012 (2)
C4	0.028 (2)	0.040 (3)	0.028 (3)	0.0039 (19)	0.0027 (19)	0.006 (2)
C5	0.035 (2)	0.027 (2)	0.024 (3)	0.0105 (18)	0.0020 (19)	0.0052 (19)
C6	0.037 (2)	0.031 (2)	0.020 (3)	0.0042 (19)	0.0016 (18)	0.0074 (19)

C7	0.033 (2)	0.035 (3)	0.024 (2)	−0.0014 (18)	−0.0006 (18)	0.0042 (19)
C8	0.037 (2)	0.032 (2)	0.022 (3)	−0.0007 (19)	0.0042 (19)	0.007 (2)
C9	0.039 (3)	0.086 (4)	0.028 (3)	−0.001 (3)	0.007 (2)	0.020 (3)
C10	0.053 (3)	0.073 (4)	0.025 (3)	0.009 (3)	0.005 (2)	0.019 (3)
C11	0.036 (2)	0.057 (3)	0.027 (3)	0.009 (2)	0.008 (2)	0.013 (2)
C12	0.036 (2)	0.049 (3)	0.031 (3)	0.003 (2)	0.0014 (19)	0.011 (2)
C13	0.035 (2)	0.039 (3)	0.025 (3)	0.0038 (19)	0.0061 (18)	0.008 (2)
C14	0.031 (2)	0.037 (3)	0.028 (3)	0.0043 (18)	−0.0003 (19)	0.003 (2)
C15	0.060 (3)	0.086 (4)	0.030 (3)	0.003 (3)	−0.010 (2)	0.025 (3)
O4	0.0445 (19)	0.102 (3)	0.031 (2)	0.0038 (19)	−0.0030 (16)	0.027 (2)
O5	0.0430 (19)	0.082 (3)	0.026 (2)	−0.0021 (17)	0.0066 (15)	0.0185 (18)
O6	0.0362 (16)	0.0478 (19)	0.0270 (19)	−0.0075 (14)	−0.0005 (13)	0.0101 (15)
N5	0.0328 (19)	0.042 (2)	0.021 (2)	−0.0054 (16)	0.0013 (16)	0.0086 (17)
N6	0.038 (2)	0.041 (2)	0.019 (2)	−0.0029 (16)	−0.0004 (16)	0.0102 (18)
N7	0.033 (2)	0.068 (3)	0.033 (2)	0.0083 (19)	0.0006 (17)	0.015 (2)
N8	0.041 (2)	0.071 (3)	0.028 (2)	−0.003 (2)	0.0023 (18)	0.009 (2)
C16	0.039 (3)	0.041 (3)	0.024 (3)	0.006 (2)	0.007 (2)	0.009 (2)
C17	0.056 (3)	0.099 (5)	0.035 (3)	0.001 (3)	0.011 (2)	0.028 (3)
C18	0.034 (2)	0.034 (3)	0.022 (3)	0.0071 (19)	0.0039 (18)	0.006 (2)
C19	0.030 (2)	0.045 (3)	0.023 (3)	0.007 (2)	−0.0037 (18)	0.009 (2)
C20	0.027 (2)	0.035 (2)	0.026 (3)	0.0004 (18)	0.0025 (18)	0.007 (2)
C21	0.030 (2)	0.028 (2)	0.021 (2)	0.0056 (17)	0.0024 (17)	0.0057 (18)
C22	0.029 (2)	0.030 (2)	0.027 (3)	0.0055 (19)	−0.0018 (18)	0.0025 (19)
C23	0.031 (2)	0.030 (2)	0.026 (3)	0.0031 (18)	0.0007 (18)	0.004 (2)
C24	0.032 (2)	0.033 (3)	0.025 (2)	0.0012 (18)	−0.0008 (18)	0.003 (2)
C25	0.041 (3)	0.087 (4)	0.030 (3)	0.007 (3)	−0.007 (2)	0.021 (3)
C26	0.047 (3)	0.074 (4)	0.027 (3)	−0.001 (3)	−0.002 (2)	0.015 (3)
C27	0.033 (2)	0.051 (3)	0.027 (3)	0.002 (2)	−0.0041 (19)	0.007 (2)
C28	0.040 (3)	0.058 (3)	0.037 (3)	−0.004 (2)	−0.002 (2)	0.023 (2)
C29	0.028 (2)	0.040 (3)	0.023 (3)	0.0053 (18)	−0.0037 (18)	0.004 (2)
C30	0.029 (2)	0.042 (3)	0.024 (3)	0.0025 (19)	0.0037 (18)	0.008 (2)

Geometric parameters (Å, º)

O1—C1	1.339 (5)	O4—C16	1.198 (5)
O1—C15	1.468 (5)	O5—C16	1.335 (5)
O2—C1	1.204 (5)	O5—C17	1.448 (5)
O3—C6	1.214 (4)	O6—C22	1.231 (5)
N1—H1	0.8600	N5—H5	0.8600
N1—N2	1.388 (4)	N5—N6	1.393 (5)
N1—C6	1.358 (5)	N5—C22	1.351 (5)
N2—C7	1.292 (5)	N6—C23	1.287 (5)
N3—C8	1.343 (5)	N7—C24	1.338 (5)
N3—C9	1.332 (5)	N7—C25	1.336 (5)
N4—C10	1.343 (6)	N8—C26	1.334 (6)
N4—C11	1.329 (5)	N8—C27	1.334 (5)
C1—C2	1.488 (6)	C16—C18	1.499 (6)
C2—C3	1.392 (6)	C17—H17A	0.9600

C2—C14	1.396 (6)	C17—H17B	0.9600
C3—H3	0.9300	C17—H17C	0.9600
C3—C4	1.383 (6)	C18—C19	1.392 (6)
C4—H4	0.9300	C18—C30	1.384 (6)
C4—C5	1.392 (5)	C19—H19	0.9300
C5—C6	1.509 (6)	C19—C20	1.384 (5)
C5—C13	1.392 (6)	C20—H20	0.9300
C7—C8	1.490 (5)	C20—C21	1.394 (5)
C7—C12	1.488 (5)	C21—C22	1.501 (6)
C8—C11	1.389 (6)	C21—C29	1.395 (6)
C9—H9	0.9300	C23—C24	1.487 (6)
C9—C10	1.366 (6)	C23—C28	1.495 (6)
C10—H10	0.9300	C24—C27	1.389 (6)
C11—H11	0.9300	C25—H25	0.9300
C12—H12A	0.9600	C25—C26	1.369 (6)
C12—H12B	0.9600	C26—H26	0.9300
C12—H12C	0.9600	C27—H27	0.9300
C13—H13	0.9300	C28—H28A	0.9600
C13—C14	1.383 (6)	C28—H28B	0.9600
C14—H14	0.9300	C28—H28C	0.9600
C15—H15A	0.9600	C29—H29	0.9300
C15—H15B	0.9600	C29—C30	1.377 (6)
C15—H15C	0.9600	C30—H30	0.9300

C1—O1—C15	115.6 (4)	C16—O5—C17	116.0 (3)
N2—N1—H1	120.5	N6—N5—H5	119.6
C6—N1—H1	120.5	C22—N5—H5	119.6
C6—N1—N2	119.1 (3)	C22—N5—N6	120.7 (4)
C7—N2—N1	115.2 (3)	C23—N6—N5	114.5 (3)
C9—N3—C8	115.7 (4)	C25—N7—C24	116.3 (4)
C11—N4—C10	115.4 (4)	C26—N8—C27	115.3 (4)
O1—C1—C2	111.8 (4)	O4—C16—O5	123.9 (4)
O2—C1—O1	123.5 (4)	O4—C16—C18	124.6 (4)
O2—C1—C2	124.7 (4)	O5—C16—C18	111.5 (4)
C3—C2—C1	118.4 (4)	O5—C17—H17A	109.5
C3—C2—C14	119.0 (4)	O5—C17—H17B	109.5
C14—C2—C1	122.5 (4)	O5—C17—H17C	109.5
C2—C3—H3	119.8	H17A—C17—H17B	109.5
C4—C3—C2	120.3 (4)	H17A—C17—H17C	109.5
C4—C3—H3	119.8	H17B—C17—H17C	109.5
C3—C4—H4	119.8	C19—C18—C16	118.4 (4)
C3—C4—C5	120.4 (4)	C30—C18—C16	121.6 (4)
C5—C4—H4	119.8	C30—C18—C19	120.0 (4)
C4—C5—C6	118.9 (4)	C18—C19—H19	120.1
C4—C5—C13	119.6 (4)	C20—C19—C18	119.8 (4)
C13—C5—C6	121.3 (4)	C20—C19—H19	120.1
O3—C6—N1	124.5 (4)	C19—C20—H20	119.7
O3—C6—C5	121.5 (4)	C19—C20—C21	120.5 (4)

N1—C6—C5	114.0 (3)	C21—C20—H20	119.7
N2—C7—C8	114.6 (3)	C20—C21—C22	118.4 (4)
N2—C7—C12	126.9 (4)	C20—C21—C29	118.9 (4)
C12—C7—C8	118.6 (4)	C29—C21—C22	122.7 (4)
N3—C8—C7	115.5 (3)	O6—C22—N5	123.6 (4)
N3—C8—C11	120.7 (4)	O6—C22—C21	121.7 (4)
C11—C8—C7	123.7 (4)	N5—C22—C21	114.7 (4)
N3—C9—H9	118.4	N6—C23—C24	115.6 (4)
N3—C9—C10	123.3 (4)	N6—C23—C28	125.5 (4)
C10—C9—H9	118.4	C24—C23—C28	118.9 (4)
N4—C10—C9	121.7 (4)	N7—C24—C23	116.1 (3)
N4—C10—H10	119.2	N7—C24—C27	120.3 (4)
C9—C10—H10	119.2	C27—C24—C23	123.6 (4)
N4—C11—C8	123.1 (4)	N7—C25—H25	118.6
N4—C11—H11	118.4	N7—C25—C26	122.7 (4)
C8—C11—H11	118.4	C26—C25—H25	118.6
C7—C12—H12A	109.5	N8—C26—C25	122.1 (4)
C7—C12—H12B	109.5	N8—C26—H26	119.0
C7—C12—H12C	109.5	C25—C26—H26	119.0
H12A—C12—H12B	109.5	N8—C27—C24	123.4 (4)
H12A—C12—H12C	109.5	N8—C27—H27	118.3
H12B—C12—H12C	109.5	C24—C27—H27	118.3
C5—C13—H13	120.1	C23—C28—H28A	109.5
C14—C13—C5	119.8 (4)	C23—C28—H28B	109.5
C14—C13—H13	120.1	C23—C28—H28C	109.5
C2—C14—H14	119.6	H28A—C28—H28B	109.5
C13—C14—C2	120.7 (4)	H28A—C28—H28C	109.5
C13—C14—H14	119.6	H28B—C28—H28C	109.5
O1—C15—H15A	109.5	C21—C29—H29	119.7
O1—C15—H15B	109.5	C30—C29—C21	120.7 (4)
O1—C15—H15C	109.5	C30—C29—H29	119.7
H15A—C15—H15B	109.5	C18—C30—H30	119.9
H15A—C15—H15C	109.5	C29—C30—C18	120.1 (4)
H15B—C15—H15C	109.5	C29—C30—H30	119.9

O1—C1—C2—C3	165.9 (4)	O4—C16—C18—C19	−9.4 (7)
O1—C1—C2—C14	−12.4 (6)	O4—C16—C18—C30	172.1 (5)
O2—C1—C2—C3	−11.9 (7)	O5—C16—C18—C19	171.3 (4)
O2—C1—C2—C14	169.9 (5)	O5—C16—C18—C30	−7.2 (6)
N1—N2—C7—C8	−179.4 (4)	N5—N6—C23—C24	−178.8 (3)
N1—N2—C7—C12	−1.0 (6)	N5—N6—C23—C28	1.9 (6)
N2—N1—C6—O3	2.5 (7)	N6—N5—C22—O6	−2.3 (6)
N2—N1—C6—C5	−176.3 (4)	N6—N5—C22—C21	175.6 (3)
N2—C7—C8—N3	154.8 (4)	N6—C23—C24—N7	−156.3 (4)
N2—C7—C8—C11	−25.7 (6)	N6—C23—C24—C27	23.7 (6)
N3—C8—C11—N4	−0.7 (7)	N7—C24—C27—N8	0.6 (7)
N3—C9—C10—N4	−0.7 (9)	N7—C25—C26—N8	0.7 (9)
C1—C2—C3—C4	−177.5 (4)	C16—C18—C19—C20	−178.7 (4)

C1—C2—C14—C13	176.4 (4)	C16—C18—C30—C29	179.5 (4)
C2—C3—C4—C5	0.6 (6)	C17—O5—C16—O4	0.5 (7)
C3—C2—C14—C13	−1.8 (6)	C17—O5—C16—C18	179.8 (4)
C3—C4—C5—C6	−176.2 (4)	C18—C19—C20—C21	−1.5 (6)
C3—C4—C5—C13	−1.0 (6)	C19—C18—C30—C29	1.1 (6)
C4—C5—C6—O3	43.3 (6)	C19—C20—C21—C22	179.9 (4)
C4—C5—C6—N1	−137.9 (4)	C19—C20—C21—C29	2.3 (6)
C4—C5—C13—C14	0.0 (6)	C20—C21—C22—O6	−21.9 (6)
C5—C13—C14—C2	1.4 (7)	C20—C21—C22—N5	160.2 (4)
C6—N1—N2—C7	179.2 (4)	C20—C21—C29—C30	−1.4 (6)
C6—C5—C13—C14	175.1 (4)	C21—C29—C30—C18	−0.3 (6)
C7—C8—C11—N4	179.8 (4)	C22—N5—N6—C23	−165.4 (4)
C8—N3—C9—C10	−0.6 (7)	C22—C21—C29—C30	−178.9 (4)
C9—N3—C8—C7	−179.3 (4)	C23—C24—C27—N8	−179.4 (4)
C9—N3—C8—C11	1.2 (6)	C24—N7—C25—C26	0.6 (8)
C10—N4—C11—C8	−0.5 (7)	C25—N7—C24—C23	178.8 (4)
C11—N4—C10—C9	1.2 (8)	C25—N7—C24—C27	−1.2 (7)
C12—C7—C8—N3	−23.8 (6)	C26—N8—C27—C24	0.7 (7)
C12—C7—C8—C11	155.8 (4)	C27—N8—C26—C25	−1.3 (8)
C13—C5—C6—O3	−131.8 (4)	C28—C23—C24—N7	23.0 (6)
C13—C5—C6—N1	47.0 (6)	C28—C23—C24—C27	−157.0 (4)
C14—C2—C3—C4	0.8 (6)	C29—C21—C22—O6	155.6 (4)
C15—O1—C1—O2	2.3 (7)	C29—C21—C22—N5	−22.3 (6)
C15—O1—C1—C2	−175.5 (4)	C30—C18—C19—C20	−0.2 (6)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O6^{i}	0.86	2.31	3.063 (5)	147
N5—H5···O3^{ii}	0.86	2.39	3.172 (5)	151
C10—H10···O4^{iii}	0.93	2.51	3.440 (7)	175
C12—H12*A*···O3^{iv}	0.96	2.38	3.327 (6)	171
C12—H12*C*···O6^{i}	0.96	2.58	3.360 (6)	139
C28—H28*A*···O3^{ii}	0.96	2.59	3.422 (6)	145

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