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N′-[(*E*)-2-Methoxybenzylidene]pyrazine-2-carbohydrazide

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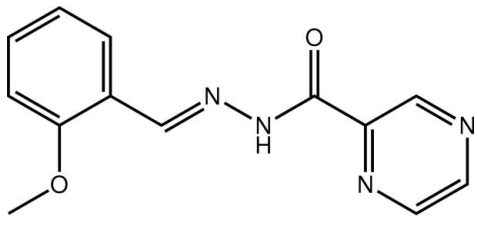
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.003 Å; R factor = 0.052; wR factor = 0.147; data-to-parameter ratio = 12.1.

In the title compound, $C_{13}H_{12}N_4O_2$, all the non-H atoms lie on a crystallographic mirror plane and an intramolecular N—H···N hydrogen bond generates an S(5) ring; the conformation about the imine bond [1.280 (3) Å] is *E*. In the crystal, molecules assemble into a two-dimensional array *via* C—H···O(carbonyl) and C—H···N(pyrazine) contacts. Layers stack along the *b*-axis direction *via* weak π–π interactions between pyrazine rings [ring centroid distance = 3.8028 (8) Å].

Related literature

For background to the anti-mycobacterial activity of pyrazinamide derivatives, see: Chaisson *et al.* (2002); Gordin *et al.* (2000); de Souza (2006); Pinheiro *et al.* (2007). For related structures of pyrazinecarbonylhydrazones, see: Baddeley *et al.* (2009); Howie *et al.* (2010*a*,*b*).



Experimental

Crystal data

$C_{13}H_{12}N_4O_2$ M_r = 256.27
Monoclinic, $P2_1/m$
a = 7.7615 (6) Å
b = 6.4257 (4) Å
c = 12.2480 (9) Å
β = 93.893 (3)°
V = 609.44 (8) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 120 K
0.46 × 0.24 × 0.01 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)
T_{min} = 0.594, T_{max} = 0.746
7850 measured reflections
1481 independent reflections
1032 reflections with $I > 2\sigma(I)$
R_{int} = 0.074

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.147
S = 1.03
1481 reflections
122 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3n···N1	0.88 (2)	2.27 (2)	2.685 (3)	109 (2)
C2—H2···O1^{i}	0.95	2.57	3.160 (3)	121
C3—H3···O1^{i}	0.95	2.44	3.103 (3)	127
C9—H9···N2^{ii}	0.95	2.56	3.437 (3)	153

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

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997), *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5910).

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N′-[(*E*)-2-Methoxybenzylidene]pyrazine-2-carbohydrazide

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S1. Comment

Pyrazinamide has well known anti-mycobacterial activity and it is the one of the most important drugs used in tuberculosis treatment (Chaisson *et al.*, 2002; Gordin *et al.*, 2000; de Souza, 2006). Various derivatives have been prepared and their anti-tuberculosis properties studied (Pinheiro *et al.*, 2007). Among the reported crystal structures of pyrazinamide derivatives are those of pyrazinecarbonylhydrazones (Baddeley *et al.*, 2009; Howie *et al.* 2010*a*, 2010*b*). In continuation of previous work, we now wish to report on the crystal structure of the title compound, (I).

All non-hydrogen atoms in (I) lie on a crystallographic mirror plane, Fig. 1. The formation of intramolecular N3—H···N1 and C6—H···O2 contacts, Table 1, contributes to the stability of the planar conformation. The configuration about the N4═C6 bond [1.280 (3) Å] is *E*. The most prominent contacts in the crystal packing are of the type C—H···O and C—H···N, Table 1. The C—H···O contacts lead to chains along the *a* direction and involve the bifurcated carbonyl-O1 atom. Chains are linked in the *c* direction by C—H···N2(pyrazinyl) contacts with the result that a two-dimensional array is formed in the *ac* plane, Fig. 2. Layers stack along the *b* direction stabilized by weak π–π interactions formed between pyrazinyl rings [ring centroid(N1,N2,C1–C4)···ring centroid(N1,N2,C1—C4)^{i} = 3.8028 (8) Å for *i*: 1 - *x*, -1/2 + *y*, 2 - *z*], Fig. 3.

S2. Experimental

Solutions of 2-pyrazinehydrazide (0.72 mmol) in water (10 ml), and 2-methoxybenzaldehyde (0.79 mmol) in ethanol (10 ml) were mixed and the reaction mixture was stirred at ambient temperature, until TLC indicated reaction was complete. The solvent was removed under reduced pressure and the residue was washed with cold diethyl ether (30 ml) and recrystallized from ethanol to yield colourless plates of (I). Yield: 52%; *M*.pt.: 453–454 K. ^{1}H NMR (400 MHz, DMSO-d6) δ: 12.35 (1*H*, s, NH), 9.26 (1*H*, s, H3), 9.00 (1*H*, s, H6), 8.92 (1*H*, s, H5), 8.80 (1*H*, s, N═CH), 7.91 (1*H*, d, J=7.5 Hz, H60), 7.45 (1*H*, t, J=7.5, H40), 7.12 (1*H*, d, J=7.5 Hz, H3′), 7.04 (1*H*, t, J=7.5 Hz, H5′), 3.87 (3*H*, s, OCH_3) p.p.m.. ^{13}C NMR (100 MHz, DMSO-d6) δ: 160.5, 148.8, 148.2, 144.7, 144.4, 143.7, 133.5, 133.2, 132.2, 128.4, 127.8, 124.1, 55.4 p.p.m. MS/ESI: [M—H]: 255. IR (KBr pellets): \v 3300 (N—H); 1680 (C═O) cm^{-1}.

S3. Refinement

The C-bound H atoms were geometrically placed (C—H = 0.95–0.98 Å) and refined as riding with U_{iso}(H) = 1.2–1.5U_{eq}(C). The N-bound atom was refined with N—H = 0.88±0.01 Å, and with U_{iso}(H) = 1.2U_{eq}(N). One reflection, *i.e.* (011), was omitted from the final refinement owing to poor agreement.

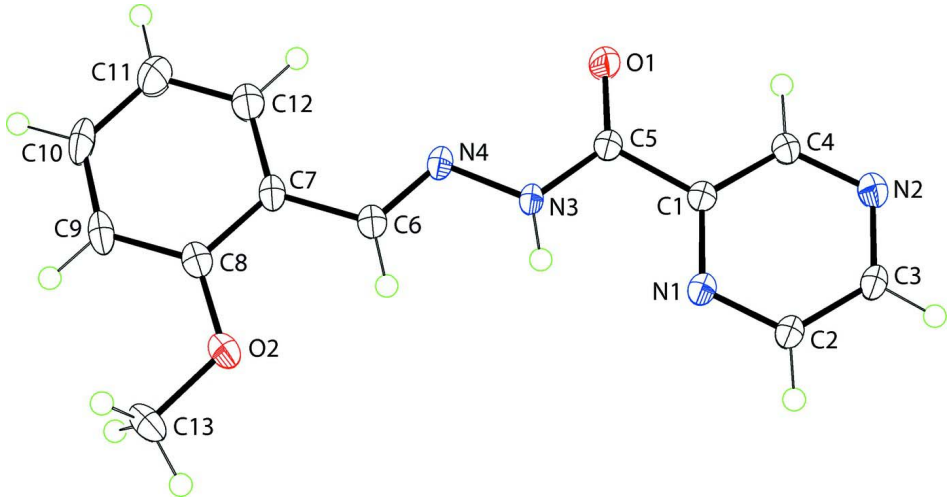

Figure 1

The molecular structure of (I) showing displacement ellipsoids at the 50% probability level.

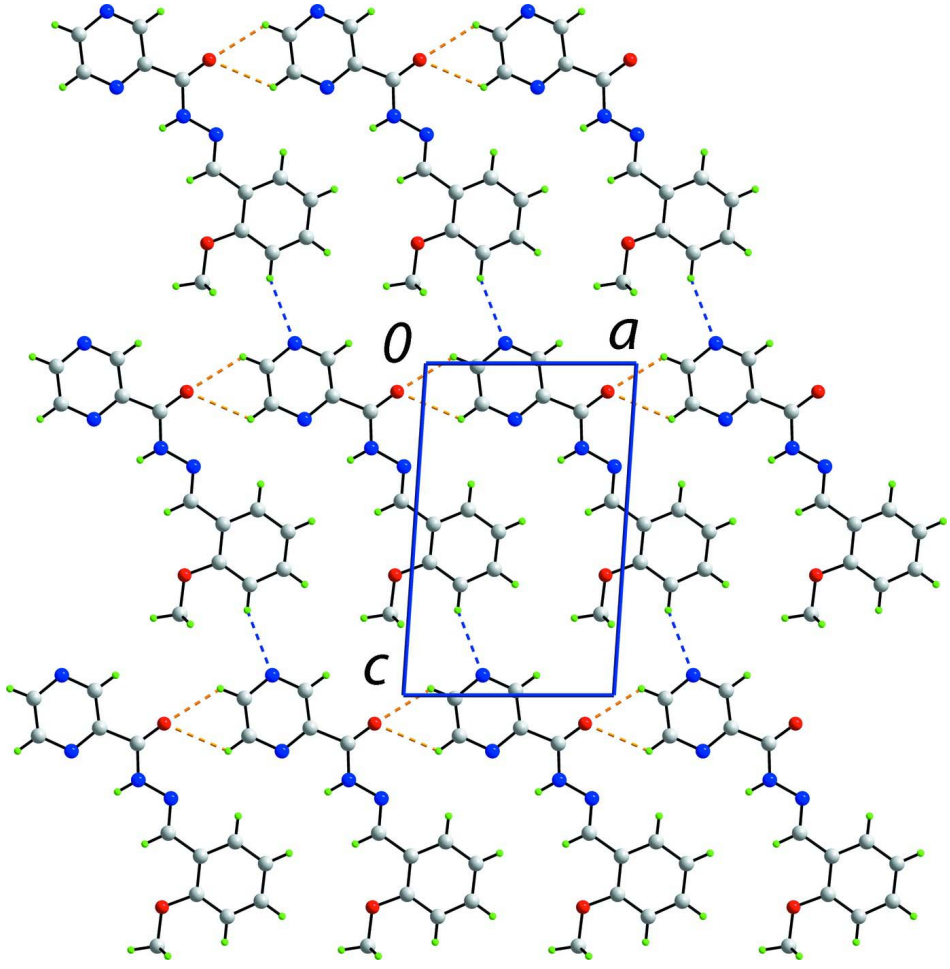

Figure 2

View of the supramolecular array in the *ac* plane in the crystal structure of (I). The C—H···O and C—H···N contacts are shown as orange and blue dashed lines, respectively.

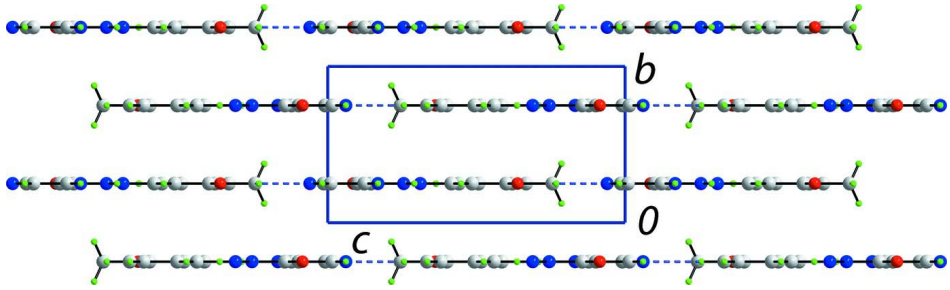

Figure 3

A view in projection down the *b* axis of the unit-cell contents of (I) with the C—H···N contacts shown as blue dashed lines.

N′-[(*E*)-2-Methoxybenzylidene]pyrazine-2-carbohydrazide

Crystal data

$C_{13}H_{12}N_4O_2$
$M_r = 256.27$
Monoclinic, $P2_1/m$
Hall symbol: -P 2yb
$a = 7.7615\ (6)$ Å
$b = 6.4257\ (4)$ Å
$c = 12.2480\ (9)$ Å
$\beta = 93.893\ (3)°$
$V = 609.44\ (8)$ Å^3
$Z = 2$
$F(000) = 268$
$D_x = 1.397$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6063 reflections
$\theta = 2.9–27.5°$
$\mu = 0.10$ mm^{-1}
$T = 120$ K
Plate, colourless
0.46 × 0.24 × 0.01 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Radiation source: Enraf Nonius FR591 rotating anode
10 cm confocal mirrors monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)
$T_{min} = 0.594$, $T_{max} = 0.746$
7850 measured reflections
1481 independent reflections
1032 reflections with $I > 2\sigma(I)$
$R_{int} = 0.074$
$\theta_{max} = 27.4°$, $\theta_{min} = 3.0°$
$h = -9\rightarrow9$
$k = -8\rightarrow8$
$l = -14\rightarrow15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.147$
$S = 1.03$
1481 reflections
122 parameters
4 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.087P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.1276 (2)	0.2500	0.91441 (14)	0.0329 (5)
O2	0.0786 (2)	0.2500	0.36159 (13)	0.0288 (5)
N1	0.5591 (2)	0.2500	0.83175 (16)	0.0220 (5)
N2	0.6293 (3)	0.2500	1.06050 (16)	0.0240 (5)
N3	0.2321 (2)	0.2500	0.74474 (15)	0.0200 (5)
H3N	0.327 (2)	0.2500	0.7099 (19)	0.024*
N4	0.0712 (2)	0.2500	0.68916 (15)	0.0193 (4)
C1	0.4324 (3)	0.2500	0.90152 (18)	0.0185 (5)
C2	0.7208 (3)	0.2500	0.87780 (19)	0.0227 (5)
H2	0.8148	0.2500	0.8320	0.027*
C3	0.7549 (3)	0.2500	0.99078 (19)	0.0235 (5)
H3	0.8717	0.2500	1.0195	0.028*
C4	0.4676 (3)	0.2500	1.01421 (18)	0.0206 (5)
H4	0.3738	0.2500	1.0602	0.025*
C5	0.2483 (3)	0.2500	0.85506 (18)	0.0199 (5)
C6	0.0729 (3)	0.2500	0.58476 (18)	0.0210 (5)
H6	0.1803	0.2500	0.5519	0.025*
C7	−0.0876 (3)	0.2500	0.51541 (19)	0.0203 (5)
C8	−0.0819 (3)	0.2500	0.40041 (19)	0.0214 (5)
C9	−0.2344 (3)	0.2500	0.3333 (2)	0.0265 (6)
H9	−0.2304	0.2500	0.2560	0.032*
C10	−0.3910 (3)	0.2500	0.3800 (2)	0.0362 (7)
H10	−0.4949	0.2500	0.3343	0.043*
C11	−0.3992 (3)	0.2500	0.4929 (2)	0.0440 (8)
H11	−0.5078	0.2500	0.5243	0.053*
C12	−0.2482 (3)	0.2500	0.5589 (2)	0.0325 (6)
H12	−0.2542	0.2500	0.6361	0.039*
C13	0.088612 (1)	0.2500	0.244660 (1)	0.0341 (6)
H13A	0.2108	0.2500	0.2292	0.051*
H13B	0.0328	0.3754	0.2135	0.051*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0181 (9)	0.0612 (11)	0.0196 (9)	0.000	0.0021 (7)	0.000
O2	0.0280 (10)	0.0415 (10)	0.0168 (9)	0.000	0.0011 (7)	0.000

N1	0.0167 (10)	0.0290 (10)	0.0200 (10)	0.000	−0.0011 (8)	0.000
N2	0.0238 (11)	0.0287 (10)	0.0190 (11)	0.000	−0.0020 (8)	0.000
N3	0.0144 (10)	0.0297 (10)	0.0154 (10)	0.000	−0.0028 (7)	0.000
N4	0.0164 (10)	0.0217 (9)	0.0191 (10)	0.000	−0.0041 (8)	0.000
C1	0.0175 (12)	0.0199 (11)	0.0180 (12)	0.000	0.0003 (9)	0.000
C2	0.0170 (11)	0.0301 (12)	0.0207 (12)	0.000	−0.0017 (9)	0.000
C3	0.0166 (12)	0.0312 (12)	0.0221 (13)	0.000	−0.0039 (10)	0.000
C4	0.0192 (12)	0.0261 (11)	0.0164 (11)	0.000	0.0002 (9)	0.000
C5	0.0176 (12)	0.0234 (11)	0.0184 (12)	0.000	−0.0004 (9)	0.000
C6	0.0205 (12)	0.0227 (11)	0.0194 (12)	0.000	−0.0008 (9)	0.000
C7	0.0218 (12)	0.0200 (11)	0.0182 (11)	0.000	−0.0049 (9)	0.000
C8	0.0257 (13)	0.0188 (11)	0.0192 (12)	0.000	−0.0015 (9)	0.000
C9	0.0339 (14)	0.0244 (12)	0.0195 (12)	0.000	−0.0102 (11)	0.000
C10	0.0234 (13)	0.0512 (16)	0.0317 (15)	0.000	−0.0145 (11)	0.000
C11	0.0200 (14)	0.079 (2)	0.0323 (16)	0.000	−0.0017 (12)	0.000
C12	0.0262 (14)	0.0484 (15)	0.0227 (13)	0.000	−0.0003 (11)	0.000
C13	0.0406 (16)	0.0459 (15)	0.0160 (13)	0.000	0.0030 (11)	0.000

Geometric parameters (Å, º)

O1—C5	1.224 (3)	C4—H4	0.9500
O2—C8	1.363 (3)	C6—C7	1.459 (3)
O2—C13	1.4395 (16)	C6—H6	0.9500
N1—C2	1.341 (3)	C7—C12	1.388 (3)
N1—C1	1.346 (3)	C7—C8	1.412 (3)
N2—C3	1.339 (3)	C8—C9	1.394 (3)
N2—C4	1.342 (3)	C9—C10	1.378 (4)
N3—C5	1.348 (3)	C9—H9	0.9500
N3—N4	1.381 (2)	C10—C11	1.388 (4)
N3—H3N	0.875 (10)	C10—H10	0.9500
N4—C6	1.280 (3)	C11—C12	1.377 (4)
C1—C4	1.389 (3)	C11—H11	0.9500
C1—C5	1.502 (3)	C12—H12	0.9500
C2—C3	1.391 (3)	C13—H13A	0.9800
C2—H2	0.9500	C13—H13B	0.9800
C3—H3	0.9500		
C8—O2—C13	117.35 (16)	N4—C6—H6	119.5
C2—N1—C1	115.86 (19)	C7—C6—H6	119.5
C3—N2—C4	115.54 (19)	C12—C7—C8	118.2 (2)
C5—N3—N4	120.89 (17)	C12—C7—C6	122.0 (2)
C5—N3—H3N	117.6 (17)	C8—C7—C6	119.8 (2)
N4—N3—H3N	121.5 (17)	O2—C8—C9	123.6 (2)
C6—N4—N3	114.97 (17)	O2—C8—C7	116.0 (2)
N1—C1—C4	121.9 (2)	C9—C8—C7	120.3 (2)
N1—C1—C5	118.47 (19)	C10—C9—C8	119.5 (2)
C4—C1—C5	119.63 (19)	C10—C9—H9	120.2
N1—C2—C3	121.9 (2)	C8—C9—H9	120.2

N1—C2—H2	119.1	C9—C10—C11	121.0 (2)
C3—C2—H2	119.1	C9—C10—H10	119.5
N2—C3—C2	122.5 (2)	C11—C10—H10	119.5
N2—C3—H3	118.8	C12—C11—C10	119.3 (2)
C2—C3—H3	118.8	C12—C11—H11	120.4
N2—C4—C1	122.4 (2)	C10—C11—H11	120.4
N2—C4—H4	118.8	C11—C12—C7	121.7 (2)
C1—C4—H4	118.8	C11—C12—H12	119.1
O1—C5—N3	124.9 (2)	C7—C12—H12	119.1
O1—C5—C1	121.5 (2)	O2—C13—H13A	108.1
N3—C5—C1	113.65 (18)	O2—C13—H13B	109.6
N4—C6—C7	121.02 (19)	H13A—C13—H13B	109.4
C5—N3—N4—C6	180.0	N4—C6—C7—C12	0.0
C2—N1—C1—C4	0.000 (1)	N4—C6—C7—C8	180.0
C2—N1—C1—C5	180.0	C13—O2—C8—C9	0.0
C1—N1—C2—C3	0.000 (1)	C13—O2—C8—C7	180.0
C4—N2—C3—C2	0.000 (1)	C12—C7—C8—O2	180.0
N1—C2—C3—N2	0.000 (1)	C6—C7—C8—O2	0.0
C3—N2—C4—C1	0.000 (1)	C12—C7—C8—C9	0.0
N1—C1—C4—N2	0.000 (1)	C6—C7—C8—C9	180.0
C5—C1—C4—N2	180.0	O2—C8—C9—C10	180.0
N4—N3—C5—O1	0.0	C7—C8—C9—C10	0.0
N4—N3—C5—C1	180.0	C8—C9—C10—C11	0.0
N1—C1—C5—O1	180.0	C9—C10—C11—C12	0.0
C4—C1—C5—O1	0.0	C10—C11—C12—C7	0.0
N1—C1—C5—N3	0.0	C8—C7—C12—C11	0.0
C4—C1—C5—N3	180.0	C6—C7—C12—C11	180.0
N3—N4—C6—C7	180.0		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3n···N1	0.88 (2)	2.27 (2)	2.685 (3)	109 (2)
C2—H2···O1^{i}	0.95	2.57	3.160 (3)	121
C3—H3···O1^{i}	0.95	2.44	3.103 (3)	127
C9—H9···N2^{ii}	0.95	2.56	3.437 (3)	153

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