IUCrData

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(7*R*)-6-Methyl-7,9-bis(prop-2-yn-1-yl)-7*H*,8*H*,9*H*-1,2,4-triazolo[4,3-*b*][1,2,4]triazepin-8-one

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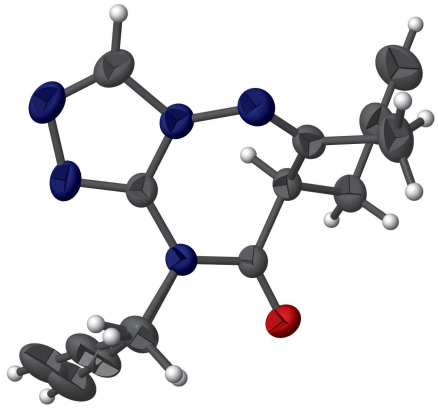
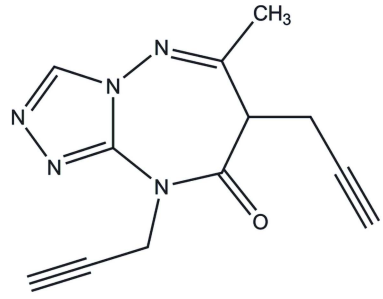
Structural data: full structural data are available from iucrdata.iucr.org

In the title molecule, $C_{12}H_{11}N_5O$, the seven-membered ring derived from triazepine adopts a boat conformation. Intermolecular C—H···N hydrogen bonds and C—H···π-ring interactions form columns of molecules parallel to the *a* axis, which are further associated into the three-dimensional crystal structure by additional C—H···O hydrogen bonds.

3D view



Chemical scheme



Structure description

Fused triazepines with a bridged nitrogen atom in heterocyclic systems exhibit interesting biological properties (Groszkowski & Wrona, 1978; Lenman *et al.*, 1997). Triazepine derivatives have also been reported to possess antifungal activity (Gupta *et al.*, 2011). As a continuation of our previous studies on the synthesis and reactivity of fused triazepines (Essassi *et al.*, 1977; Zemama *et al.*, 2009; Harmaoui *et al.*, 2015), we report the synthesis and crystal structure of the title compound (Fig. 1). A puckering analysis of the seven-membered ring yielded the parameters q_2 = 0.847 (1) Å, φ_2 = 228.47 (8)°, q_3 = 0.235 (1) Å, and φ_3 = 79.7 (3)°. These metrics indicate that the ring adopts a boat conformation.

The molecules are stacked parallel to the *a* axis through the action of intermolecular C7—H7···N4^{i} hydrogen bonds [symmetry code: (i) $1-x, 1-y, 1-z$; Table 1] and C12—H12*B*···π(*Cg*^{ii}) interactions [symmetry code: (ii) $2-x, 1-y, 1-z$; *Cg* is the centroid of the C1/C4/N1/N4/N5 ring], characterized by H12*B*···*Cg*^{ii} = 3.217 Å and C12—H12*B*···*Cg*^{ii} = 138°. Finally, intermolecular C4—H4···O1^{iii} hydrogen bonds [symmetry code: (iii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; Table 1] tie the columns together to form the full three-dimensional structure (Fig. 2).

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

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7···N4^{i}	0.98	2.40	3.164 (2)	135
C4—H4···O1^{ii}	0.93	2.23	3.147 (2)	167

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

Synthesis and crystallization

To a solution of 6-methyl-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazepin-8(9*H*)-one (0.3 g, 1.82 mmol) in *N*,*N*-dimethylformamide (10 ml), was added potassium carbonate (0.25 g, 1.82 mmol), propargyl bromide (0.14 ml, 1.82 mmol) and a catalytic amount of tetra-*n*-butylammonium bromide. The reaction mixture was stirred for 12 h. The solution was then taken to dryness under reduced pressure and the residue was extracted with dichloromethane. The precipitate formed under cooling was filtered off and recrystallized from ethanol solutionto give colourless crystals in 30% yield.

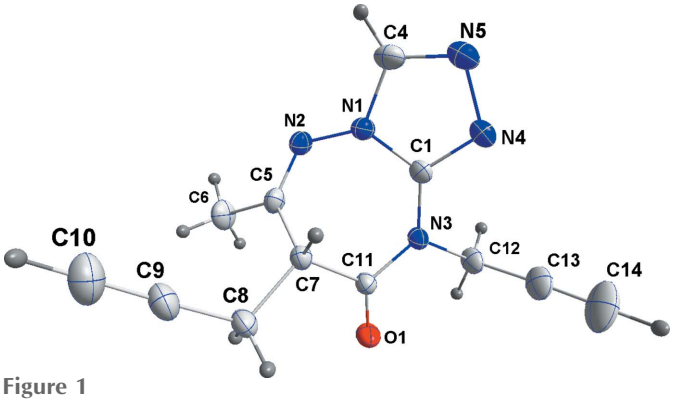


Figure 1
The title molecule with 30% probability ellipsoids for non-H atoms. Only one orientation of the disordered propynyl group C12/C13/C14 is shown.

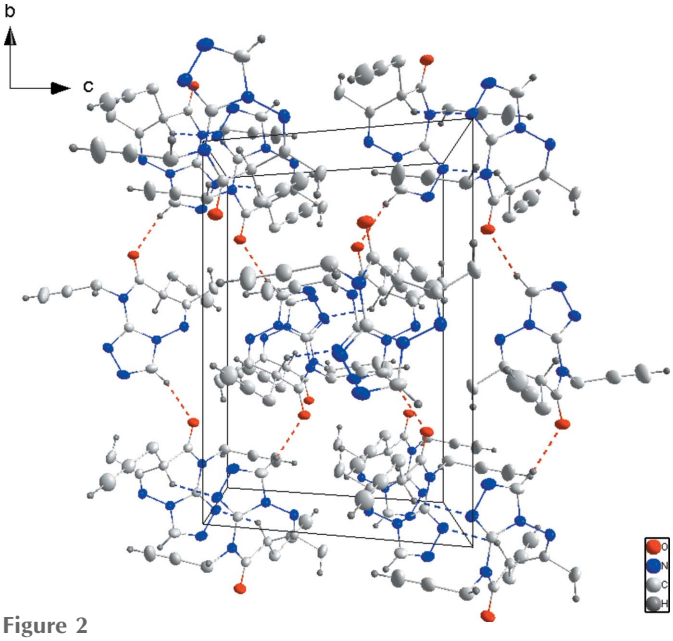


Figure 2
Packing viewed along the *a* axis with C—H···O hydrogen bonds shown as dotted lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_{11}N_5O$
M_r	241.26
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	7.5436 (3), 15.6498 (6), 10.9701 (4)
β (°)	108.334 (1)
V (Å^3)	1229.34 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.42 × 0.42 × 0.31
Data collection	
Diffractometer	Bruker *SMART APEX* CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.89, 0.97
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	23271, 3313, 2701
R_{int}	0.031
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.686
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.143, 1.05
No. of reflections	3313
No. of parameters	174
No. of restraints	28
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.49, −0.18

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The propynyl substituent attached to N3 is disordered over two sites, modelled with C12/C13/C14 [occupancy: 0.610 (15)] and C12*A*/C13*A*/C14*A* [occupancy:0.390 (15)]. The components of the disorder were refined with restraints on both the geometry and displacement parameters.

Acknowledgements

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References

Brandenburg, K. & Putz, H. (2012). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2016). *APEX3*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Essassi, E. M., Lavergne, J.-P. & Viallffont, Ph. (1977). *Tetrahedron*, **33**, 2807–2812.
Groszkowski, S. & Wrona, J. (1978). *Pol. J. Pharmacol. Pharm.* **5**, 713–715.
Gupta, M., Paul, S. & Gupta, R. (2011). *Eur. J. Med. Chem.* **46**, 631–635.
Harmaoui, A., Bouhfid, R., Essassi, E. M., Saadi, M. & El Ammari, L. (2015). *Acta Cryst.* E**71**, o1–o2.
Lenman, M. M., Lewis, A. & Gani, D. (1997). *J. Chem. Soc. Perkin Trans. 1*, pp. 2297–2312.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Zemama, R. M., Amari, I., Bouhfid, R., Essassi, E. M. & Ng, S. W. (2009). *Acta Cryst.* E**65**, o2152.

full crystallographic data

IUCrData (2016). **1**, x161245 [doi:10.1107/S2414314616012451]

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Crystal data

$C_{12}H_{11}N_5O$
M_r = 241.26
Monoclinic, $P2_1/c$
a = 7.5436 (3) Å
b = 15.6498 (6) Å
c = 10.9701 (4) Å
β = 108.334 (1)°
V = 1229.34 (8) Å^3
Z = 4
$F(000)$ = 504
D_x = 1.304 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9984 reflections
θ = 2.4–29.1°
μ = 0.09 mm^{-1}
T = 296 K
Block, colourless
0.42 × 0.42 × 0.31 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2016)
T_{min} = 0.89, T_{max} = 0.97
23271 measured reflections
3313 independent reflections
2701 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 29.2°, θ_{min} = 2.4°
h = −10→10
k = −21→21
l = −15→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.143
S = 1.05
3313 reflections
174 parameters
28 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
$w = 1/[\sigma^2(F_o^2) + (0.0829P)^2 + 0.1647P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Special details

Experimental. The diffraction data were obtained from 3 sets of 400 frames, each of width 0.5° in ω, colllected at φ = 0.00, 90.00 and 180.00° and 2 sets of 800 frames, each of width 0.45° in φ, collected at ω = –30.00 and 210.00°. The scan time was 7 sec/frame.

Refinement. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.99 Å). All were included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms. The propynyl substituent attached to N3 is disordered over two sites in a 61/39 ratio. The components of the disorder were refined with restraints that their geometries be comparable.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.53407 (14)	0.26656 (6)	0.38907 (9)	0.0503 (3)	
N1	0.54858 (14)	0.52089 (6)	0.27441 (9)	0.0370 (2)	
N2	0.46611 (15)	0.48217 (7)	0.15514 (9)	0.0403 (2)	
N3	0.66193 (13)	0.39844 (6)	0.41282 (9)	0.0364 (2)	
C1	0.64572 (15)	0.48540 (7)	0.38983 (10)	0.0338 (2)	
C4	0.5849 (2)	0.60626 (8)	0.29144 (14)	0.0477 (3)	
H4	0.5396	0.6474	0.2282	0.057*	
N4	0.73180 (15)	0.54449 (7)	0.47134 (10)	0.0434 (3)	
C5	0.37243 (15)	0.41413 (8)	0.15763 (10)	0.0366 (3)	
N5	0.69043 (17)	0.62237 (7)	0.40691 (12)	0.0508 (3)	
C6	0.3048 (2)	0.36453 (11)	0.03514 (13)	0.0561 (4)	
H6A	0.1733	0.3540	0.0149	0.084*	
H6B	0.3702	0.3111	0.0450	0.084*	
H6C	0.3274	0.3967	−0.0330	0.084*	
C7	0.33705 (15)	0.38234 (7)	0.27846 (10)	0.0336 (2)	
H7	0.3101	0.4323	0.3235	0.040*	
C8	0.17263 (17)	0.32044 (9)	0.25592 (14)	0.0477 (3)	
H8A	0.1948	0.2706	0.2103	0.057*	
H8B	0.1640	0.3016	0.3381	0.057*	
C9	−0.00402 (19)	0.36025 (11)	0.18177 (16)	0.0561 (4)	
C10	−0.1441 (2)	0.39323 (15)	0.1201 (2)	0.0803 (6)	
H10	−0.2545	0.4192	0.0715	0.096*	
C11	0.51588 (15)	0.34220 (7)	0.36473 (10)	0.0345 (2)	
C12	0.8373 (10)	0.3649 (11)	0.5031 (6)	0.0457 (7)	0.610 (15)
H12A	0.8427	0.3038	0.4902	0.055*	0.610 (15)
H12B	0.9420	0.3908	0.4835	0.055*	0.610 (15)
C13	0.8572 (15)	0.3810 (5)	0.6390 (6)	0.0565 (12)	0.610 (15)
C14	0.8738 (13)	0.3912 (7)	0.7481 (6)	0.0894 (19)	0.610 (15)
H14	0.8870	0.3992	0.8345	0.107*	0.610 (15)
C12A	0.8455 (15)	0.3695 (17)	0.4981 (8)	0.0457 (7)	0.390 (15)
H12C	0.8769	0.3151	0.4677	0.055*	0.390 (15)
H12D	0.9406	0.4106	0.4957	0.055*	0.390 (15)
C13A	0.843 (2)	0.3600 (8)	0.6311 (9)	0.0565 (12)	0.390 (15)
C14A	0.853 (2)	0.3561 (9)	0.7398 (9)	0.0894 (19)	0.390 (15)
H14A	0.8603	0.3530	0.8260	0.107*	0.390 (15)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0540 (5)	0.0310 (4)	0.0566 (5)	−0.0013 (4)	0.0044 (4)	0.0021 (4)
N1	0.0419 (5)	0.0323 (5)	0.0368 (5)	−0.0023 (4)	0.0123 (4)	0.0002 (3)
N2	0.0458 (6)	0.0431 (6)	0.0320 (5)	0.0004 (4)	0.0122 (4)	0.0007 (4)
N3	0.0315 (5)	0.0330 (5)	0.0392 (5)	−0.0002 (4)	0.0033 (4)	0.0000 (4)
C1	0.0316 (5)	0.0337 (6)	0.0362 (5)	−0.0023 (4)	0.0108 (4)	−0.0026 (4)
C4	0.0533 (7)	0.0321 (6)	0.0587 (8)	−0.0032 (5)	0.0190 (6)	0.0031 (5)
N4	0.0440 (5)	0.0382 (6)	0.0459 (6)	−0.0079 (4)	0.0109 (4)	−0.0092 (4)
C5	0.0365 (6)	0.0405 (6)	0.0307 (5)	0.0050 (4)	0.0075 (4)	−0.0036 (4)
N5	0.0528 (6)	0.0351 (6)	0.0637 (7)	−0.0073 (5)	0.0173 (6)	−0.0077 (5)
C6	0.0615 (9)	0.0670 (9)	0.0367 (6)	−0.0035 (7)	0.0108 (6)	−0.0162 (6)
C7	0.0320 (5)	0.0339 (5)	0.0328 (5)	−0.0019 (4)	0.0074 (4)	−0.0033 (4)
C8	0.0376 (6)	0.0458 (7)	0.0550 (7)	−0.0094 (5)	0.0078 (5)	−0.0014 (5)
C9	0.0356 (6)	0.0638 (9)	0.0651 (9)	−0.0079 (6)	0.0105 (6)	−0.0065 (7)
C10	0.0416 (8)	0.1020 (16)	0.0906 (14)	0.0074 (9)	0.0111 (8)	−0.0008 (11)
C11	0.0356 (5)	0.0321 (5)	0.0337 (5)	−0.0020 (4)	0.0078 (4)	−0.0024 (4)
C12	0.0305 (8)	0.0461 (15)	0.0528 (8)	0.0049 (9)	0.0024 (6)	−0.0016 (7)
C13	0.0455 (17)	0.058 (4)	0.0515 (11)	0.014 (3)	−0.0054 (11)	−0.0008 (15)
C14	0.088 (3)	0.112 (5)	0.0508 (13)	0.049 (4)	−0.0025 (14)	−0.004 (2)
C12A	0.0305 (8)	0.0461 (15)	0.0528 (8)	0.0049 (9)	0.0024 (6)	−0.0016 (7)
C13A	0.0455 (17)	0.058 (4)	0.0515 (11)	0.014 (3)	−0.0054 (11)	−0.0008 (15)
C14A	0.088 (3)	0.112 (5)	0.0508 (13)	0.049 (4)	−0.0025 (14)	−0.004 (2)

Geometric parameters (Å, º)

O1—C11	1.2117 (14)	C7—C11	1.5189 (15)
N1—C4	1.3649 (16)	C7—C8	1.5314 (16)
N1—C1	1.3657 (14)	C7—H7	0.9800
N1—N2	1.3979 (13)	C8—C9	1.4641 (19)
N2—C5	1.2830 (16)	C8—H8A	0.9700
N3—C11	1.3789 (14)	C8—H8B	0.9700
N3—C1	1.3824 (15)	C9—C10	1.179 (2)
N3—C12	1.4773 (18)	C10—H10	0.9300
N3—C12A	1.477 (2)	C12—C13	1.472 (4)
C1—N4	1.3082 (14)	C12—H12A	0.9700
C4—N5	1.2913 (19)	C12—H12B	0.9700
C4—H4	0.9300	C13—C14	1.174 (3)
N4—N5	1.3941 (16)	C14—H14	0.9300
C5—C6	1.4957 (16)	C12A—C13A	1.472 (4)
C5—C7	1.5160 (15)	C12A—H12C	0.9700
C6—H6A	0.9600	C12A—H12D	0.9700
C6—H6B	0.9600	C13A—C14A	1.174 (3)
C6—H6C	0.9600	C14A—H14A	0.9300
C4—N1—C1	104.19 (10)	C11—C7—H7	107.5
C4—N1—N2	124.30 (10)	C8—C7—H7	107.5

C1—N1—N2	129.98 (10)	C9—C8—C7	111.70 (11)
C5—N2—N1	115.21 (9)	C9—C8—H8A	109.3
C11—N3—C1	122.98 (9)	C7—C8—H8A	109.3
C11—N3—C12	118.0 (7)	C9—C8—H8B	109.3
C1—N3—C12	118.8 (7)	C7—C8—H8B	109.3
C11—N3—C12A	121.5 (11)	H8A—C8—H8B	107.9
C1—N3—C12A	115.4 (11)	C10—C9—C8	178.34 (19)
N4—C1—N1	110.63 (10)	C9—C10—H10	180.0
N4—C1—N3	125.09 (11)	O1—C11—N3	121.18 (10)
N1—C1—N3	124.09 (10)	O1—C11—C7	123.93 (10)
N5—C4—N1	111.14 (12)	N3—C11—C7	114.87 (9)
N5—C4—H4	124.4	C13—C12—N3	113.7 (6)
N1—C4—H4	124.4	C13—C12—H12A	108.8
C1—N4—N5	106.72 (10)	N3—C12—H12A	108.8
N2—C5—C6	116.50 (11)	C13—C12—H12B	108.8
N2—C5—C7	122.72 (10)	N3—C12—H12B	108.8
C6—C5—C7	120.73 (11)	H12A—C12—H12B	107.7
C4—N5—N4	107.30 (10)	C14—C13—C12	177.9 (9)
C5—C6—H6A	109.5	C13—C14—H14	180.0
C5—C6—H6B	109.5	C13A—C12A—N3	110.9 (8)
H6A—C6—H6B	109.5	C13A—C12A—H12C	109.5
C5—C6—H6C	109.5	N3—C12A—H12C	109.5
H6A—C6—H6C	109.5	C13A—C12A—H12D	109.5
H6B—C6—H6C	109.5	N3—C12A—H12D	109.5
C5—C7—C11	108.32 (9)	H12C—C12A—H12D	108.0
C5—C7—C8	115.01 (9)	C14A—C13A—C12A	175.1 (17)
C11—C7—C8	110.76 (9)	C13A—C14A—H14A	180.0
C5—C7—H7	107.5		

C4—N1—N2—C5	−151.65 (12)	N2—C5—C7—C11	−75.45 (14)
C1—N1—N2—C5	44.75 (17)	C6—C5—C7—C11	102.00 (12)
C4—N1—C1—N4	0.99 (13)	N2—C5—C7—C8	160.04 (11)
N2—N1—C1—N4	167.07 (11)	C6—C5—C7—C8	−22.50 (16)
C4—N1—C1—N3	−174.20 (11)	C5—C7—C8—C9	−61.48 (15)
N2—N1—C1—N3	−8.12 (18)	C11—C7—C8—C9	175.30 (11)
C11—N3—C1—N4	145.40 (12)	C1—N3—C11—O1	−178.44 (11)
C12—N3—C1—N4	−28.4 (3)	C12—N3—C11—O1	−4.6 (3)
C12A—N3—C1—N4	−31.9 (5)	C12A—N3—C11—O1	−1.3 (5)
C11—N3—C1—N1	−40.11 (16)	C1—N3—C11—C7	2.93 (15)
C12—N3—C1—N1	146.1 (3)	C12—N3—C11—C7	176.7 (3)
C12A—N3—C1—N1	142.6 (5)	C12A—N3—C11—C7	−179.9 (5)
C1—N1—C4—N5	−1.42 (15)	C5—C7—C11—O1	−112.30 (13)
N2—N1—C4—N5	−168.53 (11)	C8—C7—C11—O1	14.70 (16)
N1—C1—N4—N5	−0.24 (13)	C5—C7—C11—N3	66.29 (12)
N3—C1—N4—N5	174.88 (11)	C8—C7—C11—N3	−166.71 (10)
N1—N2—C5—C6	−171.81 (11)	C11—N3—C12—C13	−98.7 (11)
N1—N2—C5—C7	5.75 (16)	C1—N3—C12—C13	75.3 (11)
N1—C4—N5—N4	1.31 (16)	C11—N3—C12A—C13A	−80.7 (18)

C1—N4—N5—C4	−0.65 (15)	C1—N3—C12A—C13A	96.7 (17)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7···N4^{i}	0.98	2.40	3.164 (2)	135
C4—H4···O1^{ii}	0.93	2.23	3.147 (2)	167

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