Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

tert-Butyl *N*-{2-[*N*-(*N*,*N*′-dicyclohexylureidocarbonylethyl)carbamoyl]prop-2-yl}carbamate

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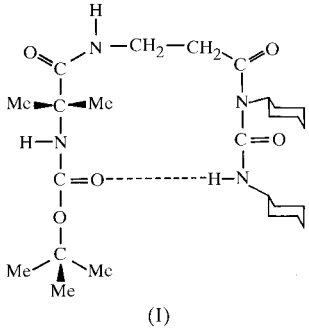
Received 7 February 2000
Accepted 18 May 2000

The title compound, $C_{25}H_{44}N_4O_5$, exhibits a turn with the main chain reversing direction, held together by an intramolecular N—H···O hydrogen bond. In the urea fragment, a notable amide C—N bond between the carboxyl C and the tertiary N atom shows marked single-bond character [1.437 (2) Å]. The dihedral angle of the β-alanyl residue, centrally located in the turn, is *gauche* [69.2 (2)°]. The packing is mediated by two intermolecular hydrogen bonds and van der Waals contacts involving the methyl moieties and the cyclohexyl rings.

Comment

Naturally occurring proteins and synthetic peptides frequently exhibit β-bend or turn conformations. The reverse turn, wherein the directionality of the polypeptide suffers a change,



(I)

has been known to play an important role in protein folding (Ptitsyn, 1981). It is well documented that the α-amino isobutyryl (Aib) residue has a high propensity for regular secondary structures such as α-helices or β-bends in designed synthetic oligopeptides (Prasad & Balaram, 1984; Karle *et al.*, 1986). The target compound, (I), was synthesized to investigate the conformation of the turn on the incorporation of an extra C atom (β-alanyl) into the main chain.

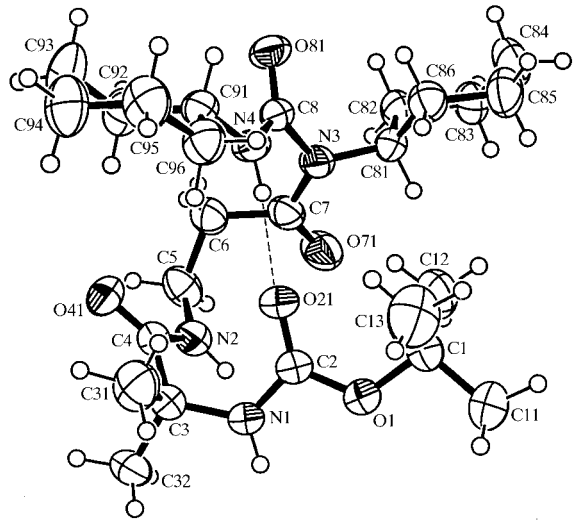


Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids (Burnett & Johnson, 1996). H atoms are shown as spheres of arbitrary radii.

The C—O and C—N bonds adjacent to the carbonyl O atoms (O21, O41, O71, O81) show partial double-bond character due to resonance with the bond lengths ranging from 1.334 (2)–1.368 (2) Å. It is important to note that the C8—N3 amide bond [1.437 (2) Å] exhibits marked single-bond character. The overall conformation of the molecule is that of a turn held together by a strong N—H···O═C hydrogen bond between N4 and O21 located at the extremities. The molecule thus forms a 13-membered ring motif (Venkatachalam, 1968; Nataraj *et al.*, 1995). The O21 atom also forms van der Waals contacts with N2 [3.147 (2) Å], coming in close proximity to C96 [3.615 (3) Å], an atom on the cyclohexyl ring. There is an additional contact between O41 and C92 of 3.588 (3) Å.

The conformation of the molecule is thus decided by free torsional rotations about N1—C3, C3—C4, N2—C5, C5—C6, C6—C7 and N3—C8. Of these, the torsion angles N1—C3—C4—N2 [39.0 (2)°] and C5—C6—C7—N3 [−155.6 (2)°] exhibit significant deviations from either the *gauche* or *trans* conformations, the rest being (−)*gauche*. In particular, the torsion angle N2—C5—C6—C7, the C-α—C-β bond of the β-alanyl residue, is 69.2 (2). This is important as the two atoms are centrally located in the turn, the reversal of direction in the chain being effected between atoms C3 and C8. Out of the four carbonyl bonds C2—N1, C4—N2, C7—N3 and C8—N4, it is only in the case of C6—C7—N3—C8 [6.9 (2)°] that the flanking C atoms, C6 and C8, are in the *cis* configuration, the rest being *trans*. There is close correspondence in the torsion angles up to C4—N2—C5—C6 from the Boc terminal end between this molecule and *t*-Boc–Aib–Aib-β-Ala–NHMe (Pavone *et al.*, 1992).

The crystal packing is mediated by the two intermolecular hydrogen bonds N1—HN1···O81 and N2—HN2···O71. In addition, there are packing interactions involving the apolar atoms of the cyclohexyl ring, the methyl groups bonded to C1 (C11, C12, C13) and C3 (C31, C32), and atoms C5 and C6.

Experimental

t-Boc–Aib–OH was coupled to β-Ala–OMe in dichloromethane using dicyclohexylcarbodiimide (DCC)/1-hydroxybenztriazole at 273–277 K for an hour. The resulting dipeptide, Boc–Aib–β-Ala–OMe, was hydrolysed using methanol/sodium hydroxide (1 *N*) at room temperature to obtain the dipeptide acid Boc–Aib–β-Ala–OH, which was then treated with DCC in *N*,*N*-dimethylformamide to give the final compound. Crystals were obtained by slow evaporation from a water/methanol mixture.

Crystal data

$C_{25}H_{44}N_4O_5$
M_r = 480.64
Triclinic, $P\overline{1}$
a = 9.9960 (10) Å
b = 10.933 (2) Å
c = 14.385 (3) Å
α = 78.13 (2)°
β = 83.740 (10)°
γ = 65.590 (10)°
V = 1400.4 (4) Å^3
Z = 2
D_x = 1.140 Mg m^{-3}
D_m = 1.14 Mg m^{-3}
D_m measured by flotation in xylene/bromoform
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10–30°
μ = 0.641 mm^{-1}
T = 293 (2) K
Plate, colourless
0.88 × 0.63 × 0.50 mm

Data collection

Enraf–Nonius CAD-4 four–circle automatic diffractometer
2ω scans
5941 measured reflections
5622 independent reflections
4579 reflections with $F_o > 4\sigma(F_o)$
R_{int} = 0.042
θ_{max} = 74.68°
$h = 0 \rightarrow 12$
$k = -12 \rightarrow 13$
$l = -15 \rightarrow 17$
3 standard reflections
every 60 reflections
frequency: 60 min
intensity decay: none

Table 1
Selected geometric parameters (Å, °).

O21—C2	1.217 (2)	O41—C4	1.222 (2)
N3—C7	1.368 (2)	N4—C8	1.334 (2)
N3—C8	1.437 (2)	N4—C91	1.461 (2)
N3—C81	1.480 (2)	N2—C4	1.339 (2)
O81—C8	1.212 (2)	N2—C5	1.441 (2)
O1—C2	1.343 (2)	O71—C7	1.222 (2)
O1—C1	1.461 (2)	C4—C3	1.540 (2)
N1—C2	1.345 (2)	C7—C6	1.502 (2)
N1—C3	1.461 (2)	C5—C6	1.513 (2)
C7—N3—C8	122.6 (1)	N4—C8—N3	113.6 (1)
C7—N3—C81	117.9 (1)	N2—C4—C3	116.3 (1)
C2—O1—C1	120.9 (1)	N1—C3—C4	110.7 (1)
C2—N1—C3	120.8 (1)	N3—C7—C6	118.3 (1)
C8—N4—C91	122.6 (1)	N2—C5—C6	112.6 (1)
C4—N2—C5	121.6 (2)	C7—C6—C5	113.3 (2)
O1—C2—N1	110.9 (1)		
C81—N3—C7—C6	−161.9 (1)	C91—N4—C8—N3	−172.7 (2)
C8—N3—C7—C6	6.9 (2)	C4—N2—C5—C6	72.9 (2)
C7—N3—C8—N4	71.2 (2)	C5—N2—C4—C3	177.2 (2)
C81—N3—C8—N4	−120.1 (2)	N2—C4—C3—N1	39.0 (2)
C1—O1—C2—N1	−179.3 (0.13)	N3—C7—C6—C5	−155.6 (2)
C3—N1—C2—O1	169.1 (1)	N2—C5—C6—C7	69.2 (2)
C2—N1—C3—C4	58.7 (2)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N4—HN4···O21	0.90 (2)	2.07 (2)	2.964 (2)	173 (2)
N1—HN1···O81^{i}	0.87 (2)	2.20 (2)	3.036 (2)	161 (2)
N2—HN2···O71^{ii}	0.88 (2)	2.17 (2)	2.906 (2)	142 (2)

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.139
S = 1.060
5622 reflections
475 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0780P)^2 + 0.1745P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.013
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0110 (8)

All the H atoms in the structure were located from difference Fourier maps [N—H 0.874 (19)–0.904 (18) Å and C—H 0.91 (3)–1.05 (3) Å], except for those bonded to C12 which were geometrically fixed (C—H 0.96 Å). Absorption corrections were not applied as the T_{max}/T_{min} ratio was 1.11, marginally greater than 1.10.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996).

The Department of Science & Technology, together with the National Diffractometer Facility at the All India Institute of Medical Sciences, New Delhi, are acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1142). Services for accessing these data are described at the back of the journal.

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supporting information

Acta Cryst. (2000). C**56**, 1120-1121 [doi:10.1107/S0108270100007447]

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Computing details

Data collection: *CAD-4 Software* (Enraf-Nonius, 1994); cell refinement: *CAD-4 Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996).

Tert-butyloxycarbonyl-alpha-amino isobutyryl - beta-Alanyl - N, (*N*,*N*′-dicyclohexyl)-urea.

Crystal data

$C_{25}H_{44}N_4O_5$
$M_r = 480.64$
Triclinic, $P\overline{1}$
$a = 9.996$ (1) Å
$b = 10.933$ (2) Å
$c = 14.385$ (3) Å
$\alpha = 78.13$ (2)°
$\beta = 83.74$ (1)°
$\gamma = 65.59$ (1)°
$V = 1400.4$ (4) Å^3
$Z = 2$
$F(000) = 524$
$D_x = 1.140$ Mg m^{-3}
$D_m = 1.14$ Mg m^{-3}
D_m measured by flotation
Cu $K\alpha$ radiation, $\lambda = 1.54180$ Å
Cell parameters from 25 reflections
$\theta = 10$–30°
$\mu = 0.64$ mm^{-1}
$T = 293$ K
Plate, colourless
0.88 × 0.63 × 0.50 mm

Data collection

CAD4 Enraf-Nonius 4-Circle automatic diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
2ω scan mode
5941 measured reflections
5622 independent reflections
4579 reflections with $Fo > 4\sigma(Fo)$
$R_{int} = 0.042$
$\theta_{max} = 74.7°$, $\theta_{min} = 3.1°$
$h = 0 \rightarrow 12$
$k = -12 \rightarrow 13$
$l = -15 \rightarrow 17$
3 standard reflections every 60 reflections
intensity decay: none

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.139$
$S = 1.06$
5622 reflections
475 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difmap and geom
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.078P)^2 + 0.1745P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.013
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Extinction correction: *SHELXL97* (Sheldrick, 1997), $Fc^{*}=kFc[1+0.001xFc^{2}\lambda^{3}/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0110 (8)

Special details

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 $F^2 > \sigma(F^2)$ 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	1.04496 (11)	0.16427 (11)	0.24617 (9)	0.0604 (3)
O21	0.94105 (11)	0.01037 (11)	0.28966 (9)	0.0576 (3)
O41	1.07630 (13)	−0.33244 (12)	0.27277 (9)	0.0658 (3)
O71	0.79771 (13)	0.05107 (13)	0.02207 (9)	0.0722 (4)
O81	0.47435 (12)	−0.02808 (13)	0.23157 (9)	0.0656 (3)
N1	1.18204 (13)	−0.05515 (13)	0.24752 (10)	0.0525 (3)
N2	1.08261 (14)	−0.18473 (14)	0.14016 (10)	0.0531 (3)
N3	0.63687 (12)	0.05533 (12)	0.14459 (9)	0.0474 (3)
N4	0.67498 (13)	−0.04871 (13)	0.30272 (9)	0.0505 (3)
C1	0.91015 (17)	0.28271 (15)	0.25973 (12)	0.0541 (4)
C2	1.04679 (15)	0.03806 (15)	0.26366 (11)	0.0479 (3)
C3	1.21767 (15)	−0.20094 (15)	0.27738 (12)	0.0518 (4)
C4	1.11566 (15)	−0.24329 (14)	0.23074 (11)	0.0483 (3)
C5	0.99364 (18)	−0.22043 (19)	0.08738 (14)	0.0606 (4)
C6	0.83328 (18)	−0.16419 (17)	0.11838 (14)	0.0587 (4)
C7	0.75842 (15)	−0.01157 (16)	0.09226 (11)	0.0514 (3)
C8	0.58792 (15)	−0.01236 (14)	0.22906 (11)	0.0475 (3)
C11	0.9567 (3)	0.4003 (2)	0.2323 (2)	0.0833 (6)
C12	0.7939 (3)	0.2974 (2)	0.1939 (2)	0.0865 (7)
C31	1.2091 (3)	−0.2385 (3)	0.38450 (15)	0.0775 (6)
C32	1.37347 (19)	−0.2783 (2)	0.2400 (2)	0.0756 (6)
C81	0.53840 (15)	0.19595 (14)	0.10291 (10)	0.0462 (3)
C82	0.45236 (18)	0.19894 (16)	0.02082 (12)	0.0542 (4)
C83	0.3702 (2)	0.34637 (17)	−0.02676 (14)	0.0633 (4)
C84	0.2677 (3)	0.4297 (2)	0.04354 (16)	0.0833 (6)
C85	0.3479 (3)	0.42160 (19)	0.12907 (17)	0.0783 (6)
C86	0.4351 (2)	0.27438 (18)	0.17612 (13)	0.0595 (4)
C91	0.65535 (16)	−0.13259 (16)	0.39191 (11)	0.0523 (4)
C92	0.7236 (2)	−0.28297 (19)	0.38511 (14)	0.0677 (5)
C93	0.7050 (4)	−0.3687 (3)	0.47946 (18)	0.0918 (7)
C94	0.7701 (3)	−0.3432 (2)	0.56020 (17)	0.0889 (7)
C95	0.7042 (3)	−0.1936 (2)	0.56670 (14)	0.0768 (5)
C96	0.7207 (2)	−0.1063 (2)	0.47236 (13)	0.0637 (4)
H12	0.8302	0.3053	0.1294	0.160 (14)*
H12A	0.7069	0.3775	0.2010	0.111 (9)*
H12B	0.7707	0.2185	0.2098	0.131 (10)*

C13	0.8604 (4)	0.2695 (3)	0.3624 (2)	0.0995 (8)
H81	0.6062 (17)	0.2402 (16)	0.0774 (11)	0.045 (4)*
H82	0.521 (2)	0.1435 (19)	−0.0272 (13)	0.060 (5)*
H82A	0.379 (2)	0.1576 (18)	0.0475 (12)	0.059 (5)*
H83	0.317 (2)	0.356 (2)	−0.0842 (16)	0.083 (6)*
HN4	0.753 (2)	−0.0263 (18)	0.2942 (12)	0.055 (4)*
H5	1.025 (2)	−0.321 (2)	0.0960 (14)	0.068 (5)*
H83A	0.444 (2)	0.385 (2)	−0.0504 (14)	0.070 (5)*
H86	0.4950 (18)	0.2693 (17)	0.2283 (12)	0.052 (4)*
H96	0.826 (2)	−0.125 (2)	0.4533 (14)	0.074 (6)*
H85	0.415 (3)	0.466 (2)	0.1113 (16)	0.085 (7)*
H86A	0.369 (2)	0.2295 (19)	0.2019 (13)	0.066 (5)*
HN1	1.254 (2)	−0.0274 (19)	0.2369 (13)	0.064 (5)*
H92	0.677 (2)	−0.297 (2)	0.3289 (16)	0.080 (6)*
H31	1.227 (3)	−0.342 (3)	0.4034 (18)	0.110 (8)*
H5A	1.006 (2)	−0.184 (2)	0.0205 (16)	0.082 (6)*
H6	0.823 (2)	−0.196 (2)	0.1862 (16)	0.073 (6)*
HN2	1.116 (2)	−0.123 (2)	0.1129 (14)	0.066 (5)*
H11	0.877 (3)	0.492 (3)	0.2398 (17)	0.105 (8)*
H91	0.550 (2)	−0.1062 (17)	0.4024 (12)	0.056 (5)*
H11A	1.035 (3)	0.387 (3)	0.2679 (19)	0.106 (9)*
H85A	0.280 (3)	0.467 (3)	0.1762 (18)	0.100 (8)*
H96A	0.677 (2)	−0.009 (2)	0.4744 (15)	0.084 (6)*
H32	1.401 (3)	−0.382 (3)	0.2590 (16)	0.091 (7)*
H92A	0.830 (3)	−0.305 (2)	0.3713 (16)	0.091 (7)*
H95	0.751 (3)	−0.178 (2)	0.6179 (17)	0.086 (7)*
H6A	0.778 (3)	−0.195 (2)	0.0840 (16)	0.091 (7)*
H84	0.218 (3)	0.531 (3)	0.0144 (18)	0.100 (7)*
H94	0.754 (3)	−0.399 (3)	0.621 (2)	0.115 (9)*
H93	0.757 (3)	−0.460 (3)	0.475 (2)	0.124 (10)*
H31A	1.277 (3)	−0.210 (3)	0.4139 (18)	0.102 (8)*
H94A	0.883 (3)	−0.374 (3)	0.5458 (19)	0.108 (9)*
H93A	0.595 (3)	−0.346 (3)	0.4952 (18)	0.101 (8)*
H84A	0.190 (3)	0.397 (3)	0.0674 (18)	0.095 (7)*
H95A	0.597 (3)	−0.171 (2)	0.5825 (17)	0.093 (7)*
H32A	1.441 (3)	−0.261 (2)	0.2705 (16)	0.087 (7)*
H11B	0.979 (3)	0.407 (3)	0.163 (2)	0.108 (9)*
H32B	1.378 (3)	−0.256 (3)	0.1758 (19)	0.100 (9)*
H31B	1.114 (3)	−0.194 (3)	0.4073 (18)	0.100 (8)*
H13	0.828 (3)	0.194 (3)	0.3800 (19)	0.104 (8)*
H13A	0.777 (3)	0.358 (3)	0.3708 (19)	0.115 (9)*
H13B	0.937 (5)	0.240 (4)	0.404 (3)	0.174 (18)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O21	0.0416 (5)	0.0556 (6)	0.0771 (8)	−0.0243 (5)	0.0075 (5)	−0.0094 (5)
N3	0.0397 (6)	0.0480 (6)	0.0487 (7)	−0.0169 (5)	−0.0046 (5)	0.0038 (5)

O81	0.0486 (6)	0.0713 (7)	0.0798 (8)	−0.0362 (5)	−0.0145 (5)	0.0134 (6)
O1	0.0457 (5)	0.0465 (6)	0.0891 (8)	−0.0206 (5)	0.0055 (5)	−0.0115 (5)
N1	0.0385 (6)	0.0476 (7)	0.0711 (8)	−0.0204 (5)	0.0034 (5)	−0.0060 (6)
O41	0.0659 (7)	0.0545 (6)	0.0794 (8)	−0.0338 (6)	−0.0089 (6)	0.0076 (5)
N4	0.0426 (6)	0.0584 (7)	0.0502 (7)	−0.0269 (6)	−0.0049 (5)	0.0069 (5)
N2	0.0452 (6)	0.0523 (7)	0.0571 (8)	−0.0176 (6)	−0.0030 (5)	−0.0035 (6)
C2	0.0418 (7)	0.0473 (7)	0.0557 (8)	−0.0209 (6)	0.0002 (6)	−0.0058 (6)
O71	0.0541 (6)	0.0726 (8)	0.0664 (8)	−0.0142 (6)	0.0094 (5)	0.0073 (6)
C8	0.0397 (6)	0.0456 (7)	0.0547 (8)	−0.0194 (6)	−0.0046 (6)	0.0030 (6)
C4	0.0398 (7)	0.0402 (7)	0.0593 (9)	−0.0134 (5)	−0.0012 (6)	−0.0029 (6)
C81	0.0449 (7)	0.0417 (7)	0.0501 (8)	−0.0188 (6)	−0.0034 (6)	−0.0001 (6)
C3	0.0419 (7)	0.0453 (7)	0.0638 (9)	−0.0161 (6)	−0.0066 (6)	−0.0006 (6)
C7	0.0408 (7)	0.0567 (8)	0.0514 (8)	−0.0166 (6)	−0.0065 (6)	−0.0017 (6)
C91	0.0445 (7)	0.0530 (8)	0.0526 (8)	−0.0209 (6)	−0.0019 (6)	0.0080 (6)
C82	0.0536 (8)	0.0454 (8)	0.0588 (9)	−0.0168 (7)	−0.0133 (7)	0.0006 (7)
C1	0.0510 (8)	0.0469 (8)	0.0609 (9)	−0.0153 (6)	−0.0003 (7)	−0.0120 (7)
C5	0.0549 (9)	0.0577 (9)	0.0627 (11)	−0.0096 (7)	−0.0043 (7)	−0.0234 (8)
C86	0.0624 (9)	0.0560 (9)	0.0553 (9)	−0.0219 (8)	0.0035 (8)	−0.0065 (7)
C6	0.0493 (8)	0.0550 (9)	0.0711 (11)	−0.0184 (7)	−0.0121 (8)	−0.0095 (8)
C83	0.0637 (10)	0.0503 (9)	0.0630 (11)	−0.0145 (8)	−0.0113 (8)	0.0046 (7)
C96	0.0701 (11)	0.0623 (10)	0.0549 (10)	−0.0263 (9)	−0.0026 (8)	−0.0024 (8)
C92	0.0798 (12)	0.0570 (10)	0.0641 (11)	−0.0290 (9)	−0.0106 (9)	0.0021 (8)
C32	0.0405 (8)	0.0585 (10)	0.124 (2)	−0.0133 (7)	−0.0047 (10)	−0.0203 (11)
C31	0.0863 (15)	0.0780 (13)	0.0654 (12)	−0.0339 (12)	−0.0231 (11)	0.0064 (10)
C84	0.0718 (12)	0.0588 (11)	0.0795 (14)	0.0021 (9)	0.0010 (10)	0.0097 (9)
C95	0.0887 (15)	0.0786 (13)	0.0504 (10)	−0.0272 (11)	−0.0052 (9)	0.0035 (9)
C11	0.0803 (14)	0.0531 (11)	0.118 (2)	−0.0281 (10)	−0.0032 (14)	−0.0162 (11)
C94	0.1117 (19)	0.0703 (13)	0.0651 (13)	−0.0264 (12)	−0.0183 (12)	0.0162 (10)
C93	0.130 (2)	0.0593 (12)	0.0827 (15)	−0.0443 (14)	−0.0155 (14)	0.0148 (10)
C85	0.0897 (14)	0.0488 (9)	0.0816 (14)	−0.0178 (9)	0.0223 (11)	−0.0147 (9)
C12	0.0782 (13)	0.0650 (12)	0.1094 (19)	−0.0209 (10)	−0.0372 (13)	0.0004 (11)
C13	0.129 (2)	0.0886 (18)	0.0775 (16)	−0.0401 (18)	0.0283 (16)	−0.0312 (13)

Geometric parameters (Å, º)

O21—C2	1.2168 (16)	C83—C84	1.511 (3)
N3—C7	1.368 (2)	C83—H83	1.00 (2)
N3—C8	1.4365 (18)	C83—H83A	0.99 (2)
N3—C81	1.4800 (18)	C96—C95	1.526 (3)
O81—C8	1.2121 (16)	C96—H96	1.01 (2)
O1—C2	1.3434 (18)	C96—H96A	0.98 (2)
O1—C1	1.4612 (18)	C92—C93	1.524 (3)
N1—C2	1.3454 (19)	C92—H92	1.05 (2)
N1—C3	1.4610 (19)	C92—H92A	0.99 (2)
N1—HN1	0.874 (19)	C32—H32	1.03 (2)
O41—C4	1.2218 (17)	C32—H32A	0.94 (2)
N4—C8	1.3342 (19)	C32—H32B	0.91 (3)
N4—C91	1.4613 (18)	C31—H31	1.05 (3)

N4—HN4	0.904 (18)	C31—H31A	1.02 (3)
N2—C4	1.339 (2)	C31—H31B	0.93 (3)
N2—C5	1.441 (2)	C84—C85	1.508 (4)
N2—HN2	0.88 (2)	C84—H84	1.02 (3)
O71—C7	1.2222 (18)	C84—H84A	0.98 (3)
C4—C3	1.540 (2)	C95—C94	1.508 (3)
C81—C86	1.521 (2)	C95—H95	0.99 (2)
C81—C82	1.522 (2)	C95—H95A	1.01 (3)
C81—H81	0.986 (16)	C11—H11	1.01 (3)
C3—C31	1.514 (3)	C11—H11A	0.93 (3)
C3—C32	1.531 (2)	C11—H11B	0.99 (3)
C7—C6	1.502 (2)	C94—C93	1.516 (4)
C91—C92	1.518 (3)	C94—H94	0.99 (3)
C91—C96	1.519 (3)	C94—H94A	1.05 (3)
C91—H91	0.974 (18)	C93—H93	0.93 (3)
C82—C83	1.522 (2)	C93—H93A	1.03 (3)
C82—H82	1.019 (19)	C85—H85	0.96 (2)
C82—H82A	1.011 (18)	C85—H85A	0.96 (3)
C1—C13	1.503 (3)	C12—H12	0.9600
C1—C11	1.506 (3)	C12—H12A	0.9600
C1—C12	1.515 (3)	C12—H12B	0.9600
C5—C6	1.513 (2)	C13—H13	0.98 (3)
C5—H5	1.00 (2)	C13—H13A	1.00 (3)
C5—H5A	0.98 (2)	C13—H13B	0.93 (4)
C86—C85	1.526 (3)	C13—C31^{i}	3.6042
C86—H86	0.988 (18)	C83—C6^{ii}	3.8540
C86—H86A	0.979 (19)	C83—C32^{iii}	3.7658
C6—H6	0.98 (2)	C84—C5^{iv}	3.8063
C6—H6A	0.97 (2)	C82—C6^{ii}	3.8422

C7—N3—C8	122.61 (12)	C84—C83—H83A	108.2 (12)
C7—N3—C81	117.87 (12)	C82—C83—H83A	107.8 (12)
C8—N3—C81	118.59 (11)	H83—C83—H83A	105.1 (16)
C2—O1—C1	120.94 (11)	C91—C96—C95	111.25 (16)
C2—N1—C3	120.78 (12)	C91—C96—H96	106.5 (12)
C2—N1—HN1	117.3 (13)	C95—C96—H96	112.8 (12)
C3—N1—HN1	118.9 (12)	C91—C96—H96A	109.6 (13)
C8—N4—C91	122.58 (12)	C95—C96—H96A	113.0 (13)
C8—N4—HN4	117.6 (11)	H96—C96—H96A	103.3 (17)
C91—N4—HN4	119.6 (11)	C91—C92—C93	110.41 (19)
C4—N2—C5	121.55 (15)	C91—C92—H92	108.9 (12)
C4—N2—HN2	118.6 (13)	C93—C92—H92	112.5 (12)
C5—N2—HN2	119.9 (13)	C91—C92—H92A	104.9 (13)
O21—C2—O1	125.22 (13)	C93—C92—H92A	109.5 (13)
O21—C2—N1	123.91 (14)	H92—C92—H92A	110.3 (18)
O1—C2—N1	110.86 (12)	C3—C32—H32	109.4 (13)
O81—C8—N4	124.88 (14)	C3—C32—H32A	109.4 (15)
O81—C8—N3	121.42 (13)	H32—C32—H32A	105.5 (19)

N4—C8—N3	113.63 (12)	C3—C32—H32B	110.1 (17)
O41—C4—N2	122.45 (15)	H32—C32—H32B	109 (2)
O41—C4—C3	121.08 (14)	H32A—C32—H32B	113 (2)
N2—C4—C3	116.27 (13)	C3—C31—H31	109.2 (14)
N3—C81—C86	113.02 (12)	C3—C31—H31A	109.4 (14)
N3—C81—C82	112.18 (12)	H31—C31—H31A	115.7 (19)
C86—C81—C82	110.57 (13)	C3—C31—H31B	110.6 (16)
N3—C81—H81	103.9 (9)	H31—C31—H31B	104 (2)
C86—C81—H81	108.6 (9)	H31A—C31—H31B	108 (2)
C82—C81—H81	108.3 (9)	C85—C84—C83	111.76 (18)
N1—C3—C31	111.11 (16)	C85—C84—H84	106.5 (14)
N1—C3—C32	107.57 (14)	C83—C84—H84	112.0 (14)
C31—C3—C32	110.30 (18)	C85—C84—H84A	106.8 (14)
N1—C3—C4	110.71 (12)	C83—C84—H84A	111.5 (15)
C31—C3—C4	110.64 (14)	H84—C84—H84A	108 (2)
C32—C3—C4	106.35 (15)	C94—C95—C96	111.36 (19)
O71—C7—N3	120.22 (14)	C94—C95—H95	110.0 (13)
O71—C7—C6	121.31 (15)	C96—C95—H95	110.4 (13)
N3—C7—C6	118.26 (14)	C94—C95—H95A	105.1 (14)
N4—C91—C92	111.29 (15)	C96—C95—H95A	109.6 (14)
N4—C91—C96	109.66 (13)	H95—C95—H95A	110.2 (19)
C92—C91—C96	110.86 (14)	C1—C11—H11	114.2 (14)
N4—C91—H91	106.7 (10)	C1—C11—H11A	111.2 (17)
C92—C91—H91	107.6 (10)	H11—C11—H11A	107 (2)
C96—C91—H91	110.7 (10)	C1—C11—H11B	105.6 (16)
C83—C82—C81	109.08 (14)	H11—C11—H11B	105 (2)
C83—C82—H82	110.3 (10)	H11A—C11—H11B	114 (2)
C81—C82—H82	110.9 (10)	C95—C94—C93	111.0 (2)
C83—C82—H82A	109.5 (10)	C95—C94—H94	110.9 (16)
C81—C82—H82A	108.2 (10)	C93—C94—H94	109.6 (16)
H82—C82—H82A	108.9 (14)	C95—C94—H94A	108.7 (15)
O1—C1—C13	109.85 (18)	C93—C94—H94A	107.5 (15)
O1—C1—C11	103.34 (14)	H94—C94—H94A	109 (2)
C13—C1—C11	110.5 (2)	C94—C93—C92	111.5 (2)
O1—C1—C12	109.71 (15)	C94—C93—H93	106.6 (19)
C13—C1—C12	112.3 (2)	C92—C93—H93	108.2 (19)
C11—C1—C12	110.74 (18)	C94—C93—H93A	108.3 (15)
N2—C5—C6	112.59 (14)	C92—C93—H93A	110.2 (14)
N2—C5—H5	111.7 (11)	H93—C93—H93A	112 (2)
C6—C5—H5	105.8 (11)	C84—C85—C86	112.09 (18)
N2—C5—H5A	106.7 (13)	C84—C85—H85	110.5 (14)
C6—C5—H5A	110.7 (13)	C86—C85—H85	108.3 (14)
H5—C5—H5A	109.4 (17)	C84—C85—H85A	110.7 (15)
C81—C86—C85	109.56 (15)	C86—C85—H85A	107.4 (15)
C81—C86—H86	108.0 (10)	H85—C85—H85A	108 (2)
C85—C86—H86	111.8 (10)	C1—C12—H12	109.5
C81—C86—H86A	108.4 (11)	C1—C12—H12A	109.5
C85—C86—H86A	110.5 (11)	H12—C12—H12A	109.5

H86—C86—H86A	108.5 (15)	C1—C12—H12B	109.5
C7—C6—C5	113.25 (15)	H12—C12—H12B	109.5
C7—C6—H6	112.0 (12)	H12A—C12—H12B	109.5
C5—C6—H6	110.3 (12)	C1—C13—H13	110.6 (16)
C7—C6—H6A	102.9 (14)	C1—C13—H13A	107.6 (16)
C5—C6—H6A	110.0 (14)	H13—C13—H13A	110 (2)
H6—C6—H6A	108.1 (18)	C1—C13—H13B	113 (3)
C84—C83—C82	110.87 (16)	H13—C13—H13B	101 (3)
C84—C83—H83	110.9 (13)	H13A—C13—H13B	115 (3)
C82—C83—H83	113.5 (13)		

C81—N3—C7—C6	−161.89 (0.14)	C4—N2—C5—C6	72.94 (0.21)
C8—N3—C7—C6	6.88 (0.22)	C5—N2—C4—C3	177.18 (0.15)
C81—N3—C7—O71	12.91 (0.22)	O41—C4—C3—N1	−145.86 (0.15)
C8—N3—C7—O71	−178.32 (0.15)	N2—C4—C3—N1	39.03 (0.19)
C8—N3—C81—C82	−98.08 (0.16)	N2—C4—C3—C32	−77.53 (0.19)
C8—N3—C81—C86	27.76 (0.19)	O41—C4—C3—C32	97.57 (0.19)
C7—N3—C8—O81	−111.62 (0.18)	N2—C4—C3—C31	162.68 (0.16)
C81—N3—C8—O81	57.07 (0.20)	O41—C4—C3—C31	−22.22 (0.23)
C7—N3—C8—N4	71.23 (0.19)	N3—C81—C86—C85	174.82 (0.15)
C81—N3—C8—N4	−120.07 (0.15)	N3—C81—C82—C83	−172.32 (0.13)
C7—N3—C81—C86	−163.01 (0.14)	C82—C81—C86—C85	−58.48 (0.19)
C7—N3—C81—C82	71.16 (0.17)	C86—C81—C82—C83	60.52 (0.18)
C1—O1—C2—O21	1.40 (0.24)	O71—C7—C6—C5	29.68 (0.24)
C2—O1—C1—C11	−179.82 (0.16)	N3—C7—C6—C5	−155.59 (0.15)
C2—O1—C1—C12	−61.68 (0.20)	N4—C91—C92—C93	178.71 (0.18)
C2—O1—C1—C13	62.25 (0.23)	N4—C91—C96—C95	−179.24 (0.16)
C1—O1—C2—N1	−179.30 (0.13)	C96—C91—C92—C93	56.38 (0.23)
C3—N1—C2—O1	169.11 (0.13)	C92—C91—C96—C95	−55.96 (0.22)
C3—N1—C2—O21	−11.59 (0.25)	C81—C82—C83—C84	−58.33 (0.20)
C2—N1—C3—C32	174.49 (0.16)	N2—C5—C6—C7	69.16 (0.20)
C2—N1—C3—C31	−64.68 (0.21)	C81—C86—C85—C84	54.81 (0.23)
C2—N1—C3—C4	58.69 (0.19)	C82—C83—C84—C85	55.36 (0.24)
C91—N4—C8—O81	10.31 (0.25)	C91—C96—C95—C94	55.30 (0.25)
C91—N4—C8—N3	−172.65 (0.13)	C91—C92—C93—C94	−56.57 (0.28)
C8—N4—C91—C96	−155.53 (0.15)	C83—C84—C85—C86	−53.72 (0.26)
C8—N4—C91—C92	81.44 (0.19)	C96—C95—C94—C93	−54.99 (0.29)
C5—N2—C4—O41	2.15 (0.25)	C95—C94—C93—C92	55.97 (0.30)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H*N*4···O21	0.90 (2)	2.07 (2)	2.964 (2)	173.39 (1.94)
N1—H*N*1···O81^{v}	0.87 (2)	2.20 (2)	3.036 (2)	161.05 (2.08)
N2—H*N*2···O71^{iii}	0.88 (2)	2.17 (2)	2.906 (2)	141.54 (1.83)

Symmetry codes: (iii) −*x*+2, −*y*, −*z*; (v) *x*+1, *y*, *z*.