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Cyclo(L-tyrosyl-L-tryptophanyl) dimethylformamide solvate

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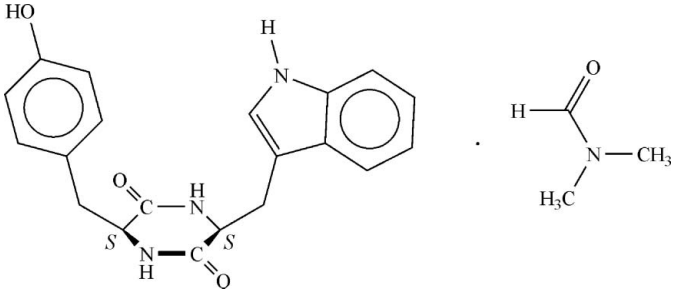
Key indicators: single-crystal X-ray study; T = 105 K; mean σ(C–C) = 0.004 Å; R factor = 0.046; wR factor = 0.123; data-to-parameter ratio = 9.4.

The structure of the title compound [systematic name: (3*S*,6*S*)-3-(4-hydroxybenzyl)-6-(1*H*-indol-3-ylmethyl)piperazine-2,5-dione dimethylformamide solvate], $C_{20}H_{19}N_3O_3\cdot C_3H_7NO$, contains hydrogen-bonded tapes typical for diketopiperazines. The structure is stabilized by strong intermolecular interactions of the types O—H···O and N—H···O involving the dipeptide and the solvent molecules. The absolute configuration was known from the starting materials.

Related literature

For related structures, see: Morris *et al.* (1974); Grant *et al.* (1999); Suguna *et al.* (1984); Lin & Webb (1973); Razak *et al.*, (2000); Luo & Palmore (2002); Görbitz (1987); Görbitz & Hartviksen (2006). Solvent inclusion: Görbitz & Hersleth (2000). Cambridge Structural Database: Allen (2002).



Experimental

Crystal data

$C_{20}H_{19}N_3O_3\cdot C_3H_7NO$
M_r = 422.48
Monoclinic, $P2_1$
a = 6.1923 (2) Å
b = 15.3873 (5) Å
c = 11.3780 (3) Å
β = 96.661 (1)°
V = 1076.81 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 105 (2) K
0.80 × 0.65 × 0.20 mm

Data collection

Siemens SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.800, T_{max} = 0.982
9514 measured reflections
2786 independent reflections
2454 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.122
S = 1.15
2786 reflections
297 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.96 (3)	1.94 (3)	2.902 (3)	174 (3)
N2—H2···O3^{ii}	0.87 (3)	2.01 (3)	2.884 (3)	178 (3)
N3—H3···O1^{iii}	0.81 (4)	2.16 (4)	2.851 (3)	144 (3)
O2—H4···O1*D*	1.04 (5)	1.59 (5)	2.606 (3)	163 (4)

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL* (Bruker, 2000); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The purchase of the diffractometer was made possible through support from the Research Council of Norway (NFR).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2058).

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supporting information

Acta Cryst. (2008). E**64**, o436 [doi:10.1107/S1600536808000640]

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S1. Comment

The title compound, (3*S*,6S)-3-(4-hydroxsybenzyl)-6 -(1*H*-indol-3-yl)methylpiperazine-2,5-dione dimethylformamide solvate, (I), was obtained as the result of an attempt to crystallize the corresponding linear dipeptide Tyr-Trp from a dimethylformamide solution. In our laboratory we have previously observed similar cyclization reactions taking place for several other dipeptides including Asp-Ala (Görbitz, 1987), Ile-Ile (Görbitz & Hartviksen, 2006) and Val-Leu (unpublished results).

The crystal structure of (I) contains straight hydrogen-bonded tapes as seen in Fig. 2. A search in the Cambridge Structural Database (CSD; Version 5.28 of November 2006; Allen 2002) revealed 59 examples of such tapes (unperturbed *e.g.* by additional cyclic connections between the two C^{α}-atoms). The periodicity of this pattern, usually corresponding to a unit-cell parameter, shows a quite narrow distribution with 54 out of 59 observations in the range 6.06 to 6.26 Å, with 6.19 Å observed for (I) being close to the 6.16 Å average value. The full range observed in the CSD is from 6.01 to 6.57 Å, with the upper limit being represented by a distinct outlier (piperazine-2,5-dione:2,5-dihydroxyterephatlic acid 1:1, Luo & Palmore, 2002).

The carbonyl O atom of the cocrystallized dimethylformamide (DMF) solvent molecule accepts a H atom from the Tyr hydroxyl group, but the DMF molecule is also involved in a number of weaker hydrogen bonds (Table 2 and Fig. 2). This is in line with previous findings that DMF molecules are often more heavily involved in intermolecular interactions than one traditionally would expect (Görbitz & Hersleth, 2000).

From the 20 naturally occurring amino acids one can construct 210 different cyclic dipeptides (as opposed to 400 linear dipeptides). Single crystal structural studies have been presented for 20 of them, including four structures with Tyr or Trp residues: *cyclo*(Gly-Trp) (Morris *et al.*, 1974), *cyclo*(Trp-Trp) DMSO solvate (Grant *et al.*, 1999), *cyclo*(Leu-Tyr) hydrate (Suguna *et al.*, 1984), and *cyclo*(Ser-Tyr) hydrate (Lin & Webb, 1973). From a conformational point of view these four peptides resemble (I) as well as each other, and all except *cyclo*(Trp-Trp) crystallize in the $P2_1$ space group. Nevertheless, each cyclic dipeptide has its own unique packing arrangement, also when all other compounds with a diketopiperazine moiety are considered.

S2. Experimental

The corresponding linear peptide Tyr-Trp was obtained from Bachem. Crystals of the cyclic analogue resulting from ring closure were obtained by slow evaporation of a solution of Tyr-Trp in dimethylformamide.

S3. Refinement

Positional parameters were refined for H atoms involved in short hydrogen bonds. Other H atoms were positioned with idealized geometry and fixed C—H distances for CH_3, CH_2, CH and aromatic CH type H-atoms at 0.98, 0.99, 1.00 and 0.95 Å, respectively; U_{iso} values were $1.2U_{eq}$ of the carrier atom or $1.5U_{eq}$ for the OH and methyl groups. In the absence

of significant anomalous scattering effects, 2334 Friedel pairs were merged. The absolute configuration was known for the purchased material.

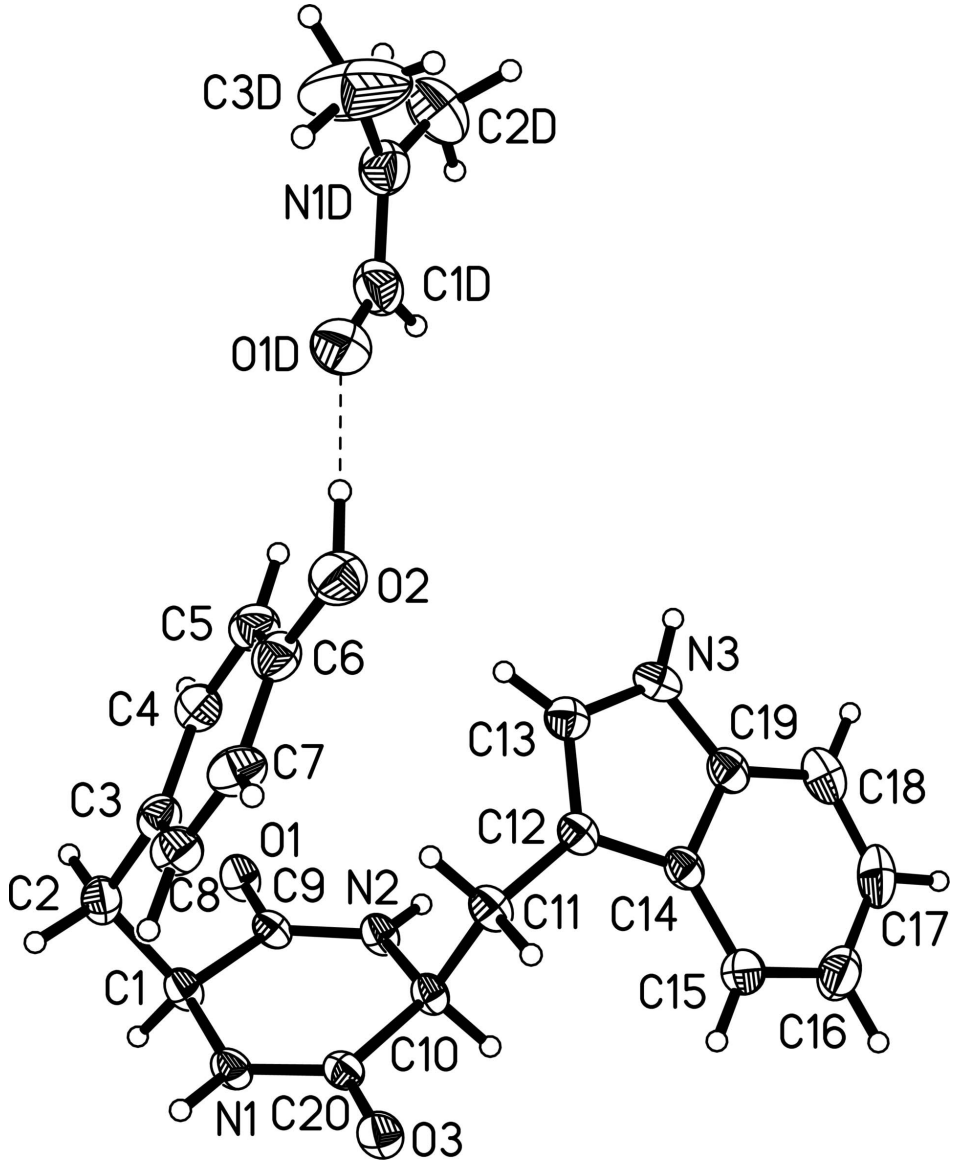

Figure 1

The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level.

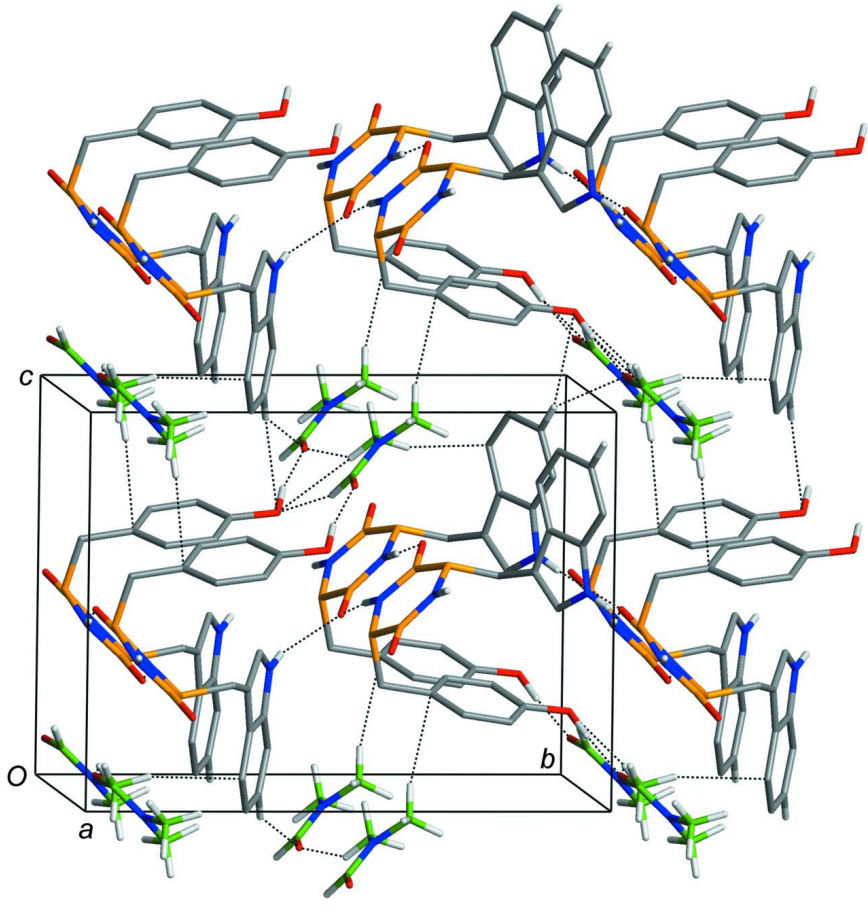

Figure 2

Crystal packing arrangement viewed approximately along the *a* axis. Hydrogen bonds and weaker interactions have been indicated by dashed lines; non-essential peptide H atoms have been left out for clarity.

(3*S*,6*S*)-3-(4-Hydroxybenzyl)-6-(1*H*-indol-3-ylmethyl)piperazine-2,5-dione dimethylformamide solvate

Crystal data

$C_{20}H_{19}N_3O_3·C_3H_7NO$
M_r = 422.48
Monoclinic, $P2_1$
Hall symbol: P 2yb
a = 6.1923 (2) Å
b = 15.3873 (5) Å
c = 11.3780 (3) Å
β = 96.661 (1)°
V = 1076.81 (6) Å^3
Z = 2
$F(000)$ = 448
D_x = 1.303 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7819 reflections
θ = 1.8–28.3°
μ = 0.09 mm^{-1}
T = 105 K
Block, colourless
0.80 × 0.65 × 0.20 mm

Data collection

Siemens SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3 pixels mm^{-1}

Sets of exposures each taken over 0.3° ω rotation scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.800, T_{max} = 0.982
9514 measured reflections
2786 independent reflections
2454 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 28.3°, θ_{min} = 1.8°
h = −8→8
k = −20→20
l = −12→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.122
S = 1.15
2786 reflections
297 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0645P)^2 + 0.2252P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.
Refinement. Data were collected by measuring three sets of exposures with the detector set at 2θ = 29°, crystal-to-detector distance 5.00 cm. Refinement of F^2 against ALL reflections.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.1720 (3)	−0.00215 (12)	0.52224 (17)	0.0277 (4)
O2	0.6882 (4)	0.38722 (14)	0.7195 (2)	0.0378 (5)
H4	0.566 (7)	0.409 (3)	0.768 (4)	0.057*
O3	0.8442 (3)	0.11985 (12)	0.31396 (17)	0.0269 (4)
N1	0.7154 (3)	0.02668 (14)	0.44228 (19)	0.0230 (4)
H1	0.867 (5)	0.014 (2)	0.465 (3)	0.028*
N2	0.2984 (3)	0.09051 (13)	0.39160 (19)	0.0223 (4)
H2	0.162 (6)	0.101 (2)	0.369 (3)	0.027*
N3	−0.0323 (4)	0.35012 (15)	0.3555 (2)	0.0268 (4)
H3	−0.123 (6)	0.379 (3)	0.383 (3)	0.032*
C1	0.5533 (4)	−0.00266 (16)	0.5160 (2)	0.0231 (5)
H11	0.5496	−0.0676	0.5117	0.028*
C2	0.6176 (4)	0.02202 (18)	0.6471 (2)	0.0280 (5)
H21	0.5086	−0.0024	0.6951	0.034*
H22	0.7596	−0.0050	0.6747	0.034*
C3	0.6339 (4)	0.11897 (18)	0.6686 (2)	0.0269 (5)
C4	0.4638 (4)	0.16582 (19)	0.7071 (2)	0.0283 (5)
H41	0.3344	0.1361	0.7206	0.034*
C5	0.4777 (4)	0.2550 (2)	0.7265 (2)	0.0317 (6)

H51	0.3601	0.2854	0.7543	0.038*
C6	0.6650 (5)	0.29970 (19)	0.7049 (2)	0.0305 (6)
C7	0.8369 (5)	0.2541 (2)	0.6663 (3)	0.0334 (6)
H71	0.9651	0.2840	0.6515	0.040*
C8	0.8222 (4)	0.1643 (2)	0.6491 (2)	0.0307 (6)
H81	0.9417	0.1336	0.6239	0.037*
C9	0.3262 (4)	0.02939 (16)	0.4750 (2)	0.0214 (4)
C10	0.4684 (4)	0.13210 (15)	0.3333 (2)	0.0203 (4)
H101	0.4283	0.1259	0.2460	0.024*
C11	0.4861 (4)	0.23024 (15)	0.3614 (2)	0.0245 (5)
H111	0.5356	0.2378	0.4467	0.029*
H112	0.5976	0.2561	0.3164	0.029*
C12	0.2766 (4)	0.27826 (15)	0.3319 (2)	0.0219 (5)
C13	0.1520 (4)	0.31262 (17)	0.4122 (2)	0.0259 (5)
H131	0.1882	0.3108	0.4956	0.031*
C14	0.1618 (4)	0.29527 (15)	0.2171 (2)	0.0236 (5)
C15	0.2022 (5)	0.27731 (19)	0.1009 (3)	0.0312 (5)
H151	0.3336	0.2499	0.0857	0.037*
C16	0.0465 (6)	0.3004 (2)	0.0084 (3)	0.0397 (7)
H161	0.0713	0.2876	−0.0706	0.048*
C17	−0.1462 (5)	0.3422 (2)	0.0292 (3)	0.0426 (7)
H171	−0.2505	0.3565	−0.0359	0.051*
C18	−0.1877 (5)	0.36285 (19)	0.1422 (3)	0.0367 (6)
H181	−0.3178	0.3919	0.1561	0.044*
C19	−0.0318 (4)	0.33969 (16)	0.2361 (2)	0.0270 (5)
C20	0.6919 (4)	0.09162 (16)	0.3637 (2)	0.0213 (4)
O1D	0.4352 (4)	0.46196 (17)	0.8569 (2)	0.0448 (5)
N1D	0.1638 (4)	0.53136 (19)	0.9359 (2)	0.0370 (5)
C1D	0.2408 (5)	0.4758 (2)	0.8623 (3)	0.0373 (6)
H1D	0.119 (6)	0.450 (3)	0.804 (3)	0.045*
C2D	−0.0661 (6)	0.5502 (2)	0.9296 (4)	0.0509 (9)
H21D	−0.1468	0.5109	0.8726	0.076*
H22D	−0.0925	0.6104	0.9041	0.076*
H23D	−0.1147	0.5419	1.0078	0.076*
C3D	0.3101 (7)	0.5866 (5)	1.0106 (5)	0.094 (2)
H31D	0.4563	0.5613	1.0191	0.141*
H32D	0.2590	0.5916	1.0887	0.141*
H33D	0.3142	0.6444	0.9747	0.141*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0200 (8)	0.0271 (9)	0.0367 (10)	0.0003 (7)	0.0066 (7)	0.0090 (7)
O2	0.0475 (12)	0.0301 (10)	0.0363 (11)	−0.0044 (9)	0.0074 (9)	−0.0026 (8)
O3	0.0188 (8)	0.0296 (9)	0.0328 (9)	0.0005 (7)	0.0059 (7)	0.0044 (8)
N1	0.0159 (9)	0.0234 (9)	0.0304 (10)	0.0030 (7)	0.0053 (7)	0.0032 (8)
N2	0.0160 (9)	0.0208 (9)	0.0303 (10)	0.0003 (7)	0.0046 (8)	0.0045 (8)
N3	0.0237 (10)	0.0212 (10)	0.0363 (12)	0.0008 (8)	0.0071 (8)	−0.0046 (9)

C1	0.0193 (10)	0.0197 (10)	0.0310 (12)	0.0015 (9)	0.0051 (9)	0.0049 (9)
C2	0.0252 (11)	0.0301 (13)	0.0286 (12)	0.0026 (10)	0.0022 (9)	0.0064 (10)
C3	0.0248 (11)	0.0320 (13)	0.0237 (11)	−0.0006 (10)	0.0014 (9)	0.0008 (10)
C4	0.0224 (11)	0.0345 (14)	0.0278 (12)	−0.0012 (10)	0.0024 (9)	0.0005 (10)
C5	0.0277 (12)	0.0385 (15)	0.0289 (13)	0.0020 (11)	0.0036 (10)	−0.0025 (11)
C6	0.0339 (14)	0.0320 (14)	0.0251 (12)	−0.0023 (11)	0.0009 (10)	−0.0020 (10)
C7	0.0279 (13)	0.0412 (15)	0.0318 (13)	−0.0059 (11)	0.0072 (10)	−0.0049 (12)
C8	0.0213 (11)	0.0400 (15)	0.0311 (13)	0.0001 (10)	0.0038 (10)	−0.0017 (11)
C9	0.0173 (10)	0.0192 (10)	0.0276 (11)	0.0019 (8)	0.0028 (8)	0.0001 (9)
C10	0.0151 (9)	0.0192 (10)	0.0266 (11)	0.0001 (8)	0.0022 (8)	0.0030 (9)
C11	0.0204 (10)	0.0192 (11)	0.0336 (13)	−0.0017 (8)	0.0027 (9)	0.0014 (9)
C12	0.0197 (10)	0.0172 (10)	0.0292 (12)	−0.0029 (8)	0.0038 (9)	0.0011 (8)
C13	0.0265 (11)	0.0215 (11)	0.0300 (12)	−0.0035 (9)	0.0049 (9)	−0.0011 (9)
C14	0.0243 (11)	0.0170 (11)	0.0296 (12)	−0.0009 (8)	0.0038 (9)	0.0020 (9)
C15	0.0367 (14)	0.0267 (12)	0.0312 (13)	0.0018 (11)	0.0080 (10)	0.0028 (10)
C16	0.0542 (19)	0.0377 (16)	0.0263 (13)	−0.0017 (13)	0.0012 (12)	0.0041 (12)
C17	0.0484 (17)	0.0380 (16)	0.0381 (15)	0.0011 (14)	−0.0087 (13)	0.0143 (13)
C18	0.0311 (13)	0.0295 (14)	0.0477 (17)	0.0020 (11)	−0.0037 (12)	0.0063 (12)
C19	0.0272 (11)	0.0194 (11)	0.0347 (13)	−0.0022 (9)	0.0046 (10)	0.0022 (10)
C20	0.0191 (10)	0.0212 (10)	0.0234 (11)	0.0023 (8)	0.0012 (8)	−0.0019 (8)
O1D	0.0433 (12)	0.0462 (13)	0.0455 (12)	0.0077 (11)	0.0076 (10)	−0.0020 (11)
N1D	0.0350 (12)	0.0415 (13)	0.0339 (12)	0.0042 (11)	0.0012 (10)	0.0027 (11)
C1D	0.0428 (16)	0.0280 (13)	0.0403 (16)	0.0007 (11)	0.0014 (13)	0.0035 (12)
C2D	0.0373 (16)	0.0400 (18)	0.075 (3)	0.0035 (13)	0.0049 (16)	0.0045 (17)
C3D	0.046 (2)	0.145 (6)	0.086 (3)	0.009 (3)	−0.013 (2)	−0.074 (4)

Geometric parameters (Å, º)

O1—C9	1.247 (3)	C10—C11	1.545 (3)
O2—C6	1.363 (4)	C10—H101	1.0000
O2—H4	1.04 (5)	C11—C12	1.497 (3)
O3—C20	1.234 (3)	C11—H111	0.9900
N1—C20	1.337 (3)	C11—H112	0.9900
N1—C1	1.453 (3)	C12—C13	1.368 (4)
N1—H1	0.96 (3)	C12—C14	1.437 (4)
N2—C9	1.333 (3)	C13—H131	0.9500
N2—C10	1.456 (3)	C14—C15	1.401 (4)
N2—H2	0.87 (3)	C14—C19	1.418 (3)
N3—C19	1.369 (4)	C15—C16	1.389 (4)
N3—C13	1.371 (3)	C15—H151	0.9500
N3—H3	0.81 (4)	C16—C17	1.399 (5)
C1—C9	1.512 (3)	C16—H161	0.9500
C1—C2	1.546 (4)	C17—C18	1.378 (5)
C1—H11	1.0000	C17—H171	0.9500
C2—C3	1.513 (4)	C18—C19	1.400 (4)
C2—H21	0.9900	C18—H181	0.9500
C2—H22	0.9900	O1D—C1D	1.231 (4)
C3—C4	1.389 (4)	N1D—C1D	1.324 (4)

C3—C8	1.397 (4)	N1D—C3D	1.445 (5)
C4—C5	1.391 (4)	N1D—C2D	1.446 (4)
C4—H41	0.9500	C1D—H1D	1.03 (4)
C5—C6	1.394 (4)	C2D—H21D	0.9800
C5—H51	0.9500	C2D—H22D	0.9800
C6—C7	1.388 (4)	C2D—H23D	0.9800
C7—C8	1.397 (4)	C3D—H31D	0.9800
C7—H71	0.9500	C3D—H32D	0.9800
C8—H81	0.9500	C3D—H33D	0.9800
C10—C20	1.520 (3)		

C6—O2—H4	108 (3)	C12—C11—H111	108.9
C20—N1—C1	126.1 (2)	C10—C11—H111	108.9
C20—N1—H1	110 (2)	C12—C11—H112	108.9
C1—N1—H1	120 (2)	C10—C11—H112	108.9
C9—N2—C10	126.4 (2)	H111—C11—H112	107.7
C9—N2—H2	112 (2)	C13—C12—C14	106.2 (2)
C10—N2—H2	121 (2)	C13—C12—C11	125.6 (2)
C19—N3—C13	108.7 (2)	C14—C12—C11	128.2 (2)
C19—N3—H3	122 (3)	C12—C13—N3	110.6 (2)
C13—N3—H3	129 (3)	C12—C13—H131	124.7
N1—C1—C9	113.6 (2)	N3—C13—H131	124.7
N1—C1—C2	111.3 (2)	C15—C14—C19	119.0 (2)
C9—C1—C2	110.1 (2)	C15—C14—C12	134.3 (2)
N1—C1—H11	107.2	C19—C14—C12	106.7 (2)
C9—C1—H11	107.2	C16—C15—C14	118.7 (3)
C2—C1—H11	107.2	C16—C15—H151	120.6
C3—C2—C1	113.7 (2)	C14—C15—H151	120.6
C3—C2—H21	108.8	C15—C16—C17	121.3 (3)
C1—C2—H21	108.8	C15—C16—H161	119.3
C3—C2—H22	108.8	C17—C16—H161	119.3
C1—C2—H22	108.8	C18—C17—C16	121.2 (3)
H21—C2—H22	107.7	C18—C17—H171	119.4
C4—C3—C8	117.9 (3)	C16—C17—H171	119.4
C4—C3—C2	121.6 (2)	C17—C18—C19	117.8 (3)
C8—C3—C2	120.5 (2)	C17—C18—H181	121.1
C3—C4—C5	121.8 (3)	C19—C18—H181	121.1
C3—C4—H41	119.1	N3—C19—C18	130.3 (3)
C5—C4—H41	119.1	N3—C19—C14	107.9 (2)
C4—C5—C6	119.7 (3)	C18—C19—C14	121.8 (3)
C4—C5—H51	120.1	O3—C20—N1	122.7 (2)
C6—C5—H51	120.1	O3—C20—C10	118.4 (2)
O2—C6—C7	117.7 (3)	N1—C20—C10	118.9 (2)
O2—C6—C5	123.0 (3)	C1D—N1D—C3D	120.3 (3)
C7—C6—C5	119.4 (3)	C1D—N1D—C2D	121.5 (3)
C6—C7—C8	120.3 (3)	C3D—N1D—C2D	117.3 (3)
C6—C7—H71	119.9	O1D—C1D—N1D	124.7 (3)
C8—C7—H71	119.9	O1D—C1D—H1D	123 (2)

C7—C8—C3	120.9 (3)	N1D—C1D—H1D	112 (2)
C7—C8—H81	119.6	N1D—C2D—H21D	109.5
C3—C8—H81	119.6	N1D—C2D—H22D	109.5
O1—C9—N2	122.6 (2)	H21D—C2D—H22D	109.5
O1—C9—C1	118.1 (2)	N1D—C2D—H23D	109.5
N2—C9—C1	119.3 (2)	H21D—C2D—H23D	109.5
N2—C10—C20	113.8 (2)	H22D—C2D—H23D	109.5
N2—C10—C11	111.9 (2)	N1D—C3D—H31D	109.5
C20—C10—C11	108.22 (19)	N1D—C3D—H32D	109.5
N2—C10—H101	107.5	H31D—C3D—H32D	109.5
C20—C10—H101	107.5	N1D—C3D—H33D	109.5
C11—C10—H101	107.5	H31D—C3D—H33D	109.5
C12—C11—C10	113.42 (19)	H32D—C3D—H33D	109.5

N1—C1—C2—C3	62.3 (3)	C14—C12—C13—N3	−0.2 (3)
C1—C2—C3—C4	97.5 (3)	C11—C12—C13—N3	−178.3 (2)
N2—C10—C11—C12	−55.4 (3)	C19—N3—C13—C12	0.7 (3)
C10—C11—C12—C13	109.8 (3)	C13—C12—C14—C15	179.9 (3)
C20—N1—C1—C9	16.1 (4)	C11—C12—C14—C15	−2.1 (4)
C20—N1—C1—C2	−108.9 (3)	C13—C12—C14—C19	−0.4 (3)
C9—C1—C2—C3	−64.6 (3)	C11—C12—C14—C19	177.6 (2)
C1—C2—C3—C8	−82.1 (3)	C19—C14—C15—C16	−2.7 (4)
C8—C3—C4—C5	−0.1 (4)	C12—C14—C15—C16	177.0 (3)
C2—C3—C4—C5	−179.7 (2)	C14—C15—C16—C17	1.1 (4)
C3—C4—C5—C6	1.2 (4)	C15—C16—C17—C18	0.8 (5)
C4—C5—C6—O2	178.6 (3)	C16—C17—C18—C19	−0.8 (5)
C4—C5—C6—C7	−1.2 (4)	C13—N3—C19—C18	176.7 (3)
O2—C6—C7—C8	−179.7 (3)	C13—N3—C19—C14	−1.0 (3)
C5—C6—C7—C8	0.1 (4)	C17—C18—C19—N3	−178.3 (3)
C6—C7—C8—C3	1.0 (4)	C17—C18—C19—C14	−0.9 (4)
C4—C3—C8—C7	−1.0 (4)	C15—C14—C19—N3	−179.4 (2)
C2—C3—C8—C7	178.6 (3)	C12—C14—C19—N3	0.9 (3)
C10—N2—C9—O1	178.7 (2)	C15—C14—C19—C18	2.7 (4)
C10—N2—C9—C1	−0.4 (4)	C12—C14—C19—C18	−177.1 (2)
N1—C1—C9—O1	170.0 (2)	C1—N1—C20—O3	171.3 (2)
C2—C1—C9—O1	−64.4 (3)	C1—N1—C20—C10	−9.2 (4)
N1—C1—C9—N2	−10.8 (3)	N2—C10—C20—O3	176.5 (2)
C2—C1—C9—N2	114.7 (2)	C11—C10—C20—O3	−58.4 (3)
C9—N2—C10—C20	7.7 (3)	N2—C10—C20—N1	−3.0 (3)
C9—N2—C10—C11	−115.4 (3)	C11—C10—C20—N1	122.1 (2)
C20—C10—C11—C12	178.4 (2)	C3D—N1D—C1D—O1D	5.3 (6)
C10—C11—C12—C14	−67.9 (3)	C2D—N1D—C1D—O1D	174.1 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.96 (3)	1.94 (3)	2.902 (3)	174 (3)
N2—H2···O3^{ii}	0.87 (3)	2.01 (3)	2.884 (3)	178 (3)

N3—H3···O1^{iii}	0.81 (4)	2.16 (4)	2.851 (3)	144 (3)
O2—H4···O1*D*	1.04 (5)	1.59 (5)	2.606 (3)	163 (4)
C1*D*—H1*D*···O2^{ii}	1.03 (4)	2.89 (4)	3.862 (4)	158
C2*D*—H21*D*···O1*D*^{ii}	0.98	2.68	3.387 (4)	129
C2*D*—H21*D*···O2^{ii}	0.98	2.70	3.671 (4)	171
C2*D*—H22*D*···C15^{iii}	0.98	2.66	3.602 (4)	163
C3*D*—H32*D*···C3^{iv}	0.98	2.80	3.660 (4)	147

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