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(3*R*)-Methyl 6-*tert*-butoxycarbonylamino-5-oxo-2,3-dihydro-5*H*-1,3-thiazolo[3,2-*a*]pyridine-3-carboxylate

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The absolute configuration has been determined for the title compound, $C_{14}H_{18}N_2O_5S$, a bicyclic aromatic building block which can act as a rigid fluorescence marker in peptide backbones. In the crystal packing, the two independent molecules of the asymmetric unit are aligned in an antiparallel manner as dimers which are stabilized by antiparallel intermolecular N—H···O═C hydrogen bonds. In addition, there are weak intermolecular C—H···O interactions.

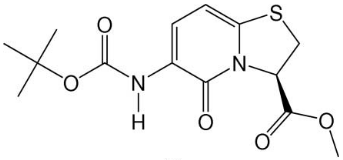
Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.002 Å
R factor = 0.034
wR factor = 0.086
Data-to-parameter ratio = 18.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

β-Sheets and β-turns are important structural elements in peptide chemistry. Monocyclic (Phillips *et al.*, 2002) or bicyclic (Tremmel & Geyer, 2004; Nagai & Sato, 1985) building blocks are introduced in peptide strands to stabilize secondary structures.



(I)

The title compound, (I), was prepared in a few steps, starting with the condensation of D-aldurono-2,5-lactone and L-cysteine methyl ester hydrochloride, followed by the elimination of two molecules of water (Tremmel *et al.*, 2003; Tremmel & Geyer, 2005). The antiparallel orientation of the two molecules of the asymmetric unit represents a mini-β-sheet with two antiparallel intermolecular hydrogen bonds. A similar relative alignment was observed in cyclic hexapeptides which contain two bicyclic dipeptides (Tremmel & Geyer, 2004). In addition, a three-dimensional network is formed *via* weak C—H···O hydrogen bonds (see Table 2 for hydrogen-bond parameters).

No antiparallel hydrogen bonds were observed in the crystal structure of (1*R*,3*R*)-methyl-6-*tert*-butoxycarbonylamino-1,5-dioxo-2,3-dihydro-5*H*-1,3-thiazolo[3,2-*a*]pyridine-3-carboxylate (Seger *et al.*, 2005). This sulfoxide can easily be prepared by oxidation of the title compound.

Experimental

The title compound was prepared by treatment of (3*R*,7*R*,8*S*,8a*S*)-methyl 6-*tert*-butoxycarbonylamino-7,8-dihydroxy-5-oxohexahydro-5*H*-[1,3]thiazolo[3,2-*a*]pyridine-3-carboxylate (5.0 g, 13.9 mmol) with triethylamine (6.7 ml, 48.6 mmol) and methanesulfonyl chloride (3.2 ml, 41.7 mmol) in a mixture of dichloromethane and pyridine (1:1 (*v*/*v*), 60 ml). After column chromatography, the title compund was isolated (yield: 4.1 g, 12.6 mmol, 91%). Single crystals were

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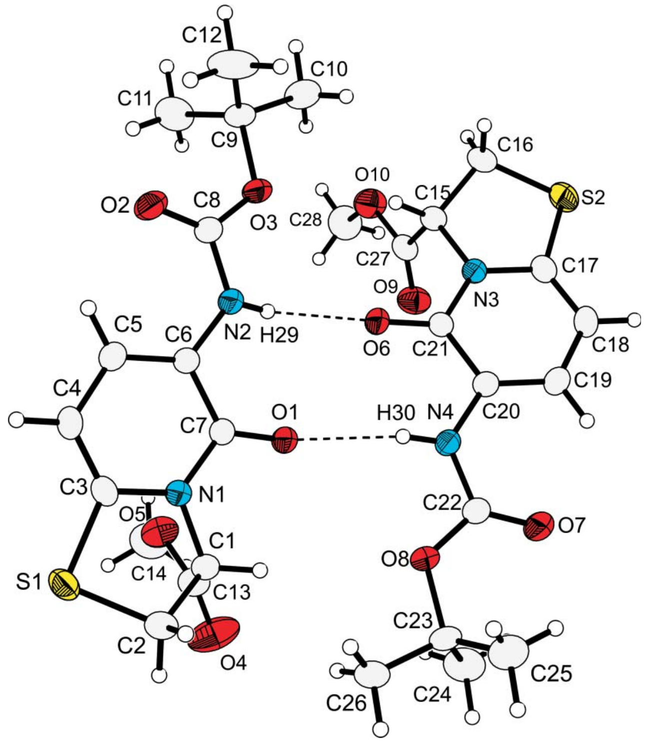

Figure 1
The asymmetric unit of the title compound with the atom-numbering scheme. Dashed lines indicate N—H···O hydrogen bonds. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

obtained by recrystallization from ethyl acetate/petroleum ether. ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.74 (*d*, $^3J_{7,8}$ = 7.74 Hz, 1H, 7-H), 7.72 (*s*, 1H, NH), 6.30 (*d*, $^3J_{8,7}$ = 7.81 Hz, 1H, 8-H), 5.61 (*dd*, $^3J_{3,2}t$ = 8.74 Hz, $^3J_{3,2}h$ = 1.94 Hz, 1H, 3H), 3.92 (*dd*, $^2J_2t_{,2}h$ = 12.04 Hz, $^3J_2t_{,3}$ = 8.74 Hz, 1H, 2-H^t), 3.71 (*s*, 3H, OMe), 3.61 (*dd*, $^2J_2h_{,2}t$ = 12.04 Hz, $^3J_2h_{,3}$ = 1.94 Hz, 1H, 2-H^h), 1.44 (*s*, 9H, *t*Bu—H).

Crystal data

$C_{14}H_{18}N_2O_5S$
M_r = 326.37
Monoclinic, $P2_1$
a = 11.9054 (8) Å
b = 10.8101 (6) Å
c = 13.6064 (9) Å
β = 112.957 (7)°
V = 1612.4 (2) Å^3
Z = 4

D_x = 1.344 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8000 reflections
θ = 2.7–28.0°
μ = 0.23 mm^{-1}
T = 173 K
Prism, colourless
0.60 × 0.48 × 0.28 mm

Data collection

Stoe IPDS diffractometer
ω scans
27858 measured reflections
7579 independent reflections
7361 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.026
$\theta_{\rm max}$ = 28.0°
$h = -15 \rightarrow 15$
$k = -14 \rightarrow 14$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.086
S = 1.07
7579 reflections
412 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0708P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.002
$\Delta\rho_{\rm max}$ = 0.33 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.26 e Å^{-3}
Absolute structure: Flack (1983), 3605 Friedel pairs
Flack parameter: 0.01 (3)

Table 1
Selected geometric parameters (Å, °).

S1—C2	1.8274 (17)	N1—C7	1.3811 (16)
S1—C3	1.7558 (13)	N2—C6	1.4064 (16)
S2—C16	1.8158 (17)	N2—C8	1.3647 (17)
S2—C17	1.7485 (13)	N3—C17	1.3786 (19)
O1—C7	1.2405 (17)	N3—C21	1.3831 (15)
O2—C8	1.2111 (19)	N3—C15	1.4595 (17)
O3—C9	1.4838 (18)	N4—C22	1.3623 (17)
O3—C8	1.3463 (17)	N4—C20	1.4052 (16)
O6—C21	1.2330 (17)	C1—C13	1.5263 (19)
O7—C22	1.2122 (18)	C1—C2	1.531 (2)
O8—C23	1.478 (2)	C3—C4	1.346 (2)
O8—C22	1.3459 (17)	C4—C5	1.4184 (19)
N1—C1	1.4617 (17)	C5—C6	1.375 (2)
N1—C3	1.3774 (19)	C6—C7	1.4550 (18)
C2—S1—C3	90.63 (7)	O1—C7—C6	124.90 (11)
C16—S2—C17	91.59 (7)	N1—C7—C6	114.86 (12)
C8—O3—C9	118.87 (12)	O1—C7—N1	120.23 (12)
C22—O8—C23	118.74 (12)	O2—C8—O3	125.05 (12)
C3—N1—C7	124.90 (11)	O3—C8—N2	110.53 (12)
C1—N1—C3	114.93 (10)	O2—C8—N2	124.42 (13)
C1—N1—C7	120.06 (11)	N3—C15—C16	105.85 (11)
C6—N2—C8	124.10 (12)	S2—C16—C15	106.07 (10)
C15—N3—C21	119.13 (11)	S2—C17—N3	111.73 (10)
C17—N3—C21	124.81 (11)	N3—C17—C18	119.76 (12)
C15—N3—C17	115.62 (10)	S2—C17—C18	128.50 (12)
C20—N4—C22	123.96 (12)	C17—C18—C19	118.76 (15)
N1—C1—C2	105.77 (12)	C18—C19—C20	121.62 (13)
S1—C2—C1	104.53 (10)	C19—C20—C21	120.08 (11)
N1—C3—C4	119.97 (12)	N4—C20—C19	127.06 (12)
S1—C3—C4	128.34 (12)	N4—C20—C21	112.86 (11)
S1—C3—N1	111.68 (10)	N3—C21—C20	114.81 (12)
C3—C4—C5	118.88 (14)	O6—C21—C20	124.77 (11)
C4—C5—C6	121.52 (13)	O6—C21—N3	120.39 (11)
N2—C6—C5	126.37 (12)	O7—C22—N4	124.70 (13)
N2—C6—C7	113.82 (12)	O7—C22—O8	125.25 (13)
C5—C6—C7	119.80 (11)	O8—C22—N4	110.03 (12)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H29···O6	0.78 (3)	2.19 (3)	2.9539 (17)	167 (2)
N4—H30···O1	0.85 (2)	2.20 (2)	3.0346 (16)	170 (2)
C4—H4···O7$^{\rm i}$	0.95	2.34	3.218 (2)	154
C16—H16A···O6$^{\rm ii}$	0.99	2.49	3.1799 (17)	127
C16—H16A···O9$^{\rm ii}$	0.99	2.53	3.3085 (18)	136
C18—H18···O2$^{\rm iii}$	0.95	2.45	3.250 (2)	142

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

C-bonded H atoms were refined with idealized geometry [C—H = 0.95–0.99 Å, H—C—H = 109.5° and $U_{\rm iso}$ (H) = 1.2$U_{\rm eq}$(C)]. N-bonded H atoms were located and refined isotropically; the bond lengths are 0.78 (3) and 0.85 (2) Å.

Data collection: *IPDS* (Stoe & Cie, 1998); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2004); software used to prepare material for publication: *PLATON* (Spek, 2003).

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.

Brandenburg, K. (2004). *DIAMOND*. Version 3.0a. Crystal Impact GbR, Bonn, Germany.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Nagai, U. & Sato, K. (1985). *Tetrahedron Lett.* **26**, 647–650.
Phillips, S. T., Rezac, M., Abel, U., Kossenjans, M. & Bartlett, P. A. (2002). *J. Am. Chem. Soc.* **124**, 58.
Seger, H., Marsch, M., Geyer, A. & Harms, K. (2005). *Acta Cryst.* E**61**, o1798–o1799.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Stoe & Cie (1998). *IPDS*. Version 2.89. Stoe & Cie GmbH, Darmstadt, Germany.
Tremmel, P. & Geyer, A. (2004). *Angew. Chem.* **116**, 5913–5915.
Tremmel, P., Brand, J., Knapp, V. & Geyer, A. (2003). *Eur. J. Org. Chem.* pp. 878–884.
Tremmel, P. & Geyer, A. (2005). *Eur. J. Org. Chem.* In the press.