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(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

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Key indicators

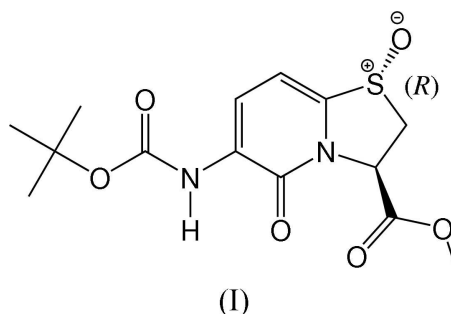
Single-crystal X-ray study
 $T = 193$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.024
 wR factor = 0.057
Data-to-parameter ratio = 10.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**(1*R*,3*R*)-Methyl 6-*tert*-butoxycarbonylamino-
1,5-dioxo-2,3-dihydro-5*H*-1,3-thiazolo[3,2-*a*]-
pyridine-3-carboxylate**

The absolute configuration has been determined for the title compound, $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_6\text{S}$, a fluorescent dipeptide analogue, which can act as a rigid backbone chromophore in peptides. Intermolecular $\text{N}-\text{H}\cdots\text{O}=\text{C}$ hydrogen bonds [$\text{H}\cdots\text{O} = 2.37$ (2) Å] are observed in the crystal packing.

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Comment

Bicyclic dipeptide mimetics are well known for inducing and stabilizing certain secondary structures, *i.e.* β -turns (Nagai & Sato, 1985; Tremmel & Geyer, 2004), in peptide strands.



The title compound, (I), was prepared by oxidation of methyl (3*R*)-6-*tert*-butoxycarbonylamino-5-oxo-2,3-dihydro-5*H*-1,3-thiazolo[3,2-*a*]pyridine-3-carboxylate, which can easily be synthesized, starting from L-cysteine methylester hydrochloride and D- γ -glucuronolactone, finally followed by elimination of two molecules of water (Tremmel *et al.*, 2003; Tremmel & Geyer, 2005). In order to investigate the influence of the sulfur on the fluorescence properties of this compound, it was oxidized using *m*-CPBA to yield the two possible diastereomeric sulfoxides and the corresponding sulfone. The NMR spectroscopy of the diastereomeric sulfoxides was not conclusive but crystals of (I) could be obtained to identify both diastereomers.

In the crystal structure, molecules are connected into one-dimensional chains along the *b* axis *via* $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds. In addition, a three-dimensional network is formed *via* weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds (see Table 2 for hydrogen-bond geometries).

Experimental

The reaction of methyl (3*R*)-6-*tert*-butoxycarbonylamino-5-oxo-2,3-dihydro-5*H*-1,3-thiazolo[3,2-*a*]pyridine-3-carboxylate with 1 equivalent of *m*-CPBA in ethyl acetate at 273 K yielded the diastereomeric

mixture of the title compound and the (1*S*,3*R*) diastereomer in a ratio of 1:2.3. (I) was recrystallized from ethanol. ¹H NMR (600 MHz, DMSO-*d*₆): δ 8.20 (*s*, 1H, NH), 8.03 (*d*, ³*J*_{7,8} = 7.7 Hz, 1H, 7-H), 7.1 (*d*, ³*J*_{8,7} = 7.7 Hz, 1H, 8H), 5.61 (*dd*, ³*J*_{3,2'} = 6.3 Hz, ³*J*_{3,2''} = 7.4 Hz, 1-H, 3-H), 3.89 (*dd*, ³*J*_{2',3} = 6.3 Hz, ³*J*_{2',2''} = 13.6 Hz, 1H, 2'-H), 3.72 (*dd*, ³*J*_{2',3} = 7.4 Hz, ³*J*_{2',2''} = 13.6 Hz, 1H, 2''-H), 3.71 (*s*, 3H, OMe), 1.46 (*s*, 9H, *t*Bu).

Crystal data

C₁₄H₁₈N₂O₆S
M_r = 342.36
 Monoclinic, *P*2₁
a = 11.4352 (15) Å
b = 6.1405 (5) Å
c = 11.5469 (14) Å
 β = 97.785 (15)°
V = 803.33 (16) Å³
Z = 2

D_x = 1.415 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 5921 reflections
 θ = 1.7–25°
 μ = 0.23 mm⁻¹
T = 193 (2) K
 Plate, colourless
 0.41 × 0.22 × 0.09 mm

Data collection

Stoe IPDS-2 diffractometer
 ω scans
 Absorption correction: none
 5976 measured reflections
 2931 independent reflections
 2665 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.024
 θ_{\max} = 26.1°
h = -13 → 14
k = -7 → 7
l = -14 → 13

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.024
wR (*F*²) = 0.057
S = 0.99
 2931 reflections
 280 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} < 0.001
 $\Delta\rho_{\max} = 0.18 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.19 \text{ e } \text{Å}^{-3}$
 Absolute structure: Flack (1983),
 with 1222 Friedel pairs
 Flack parameter = 0.01 (6)

Table 1

Selected geometric parameters (Å, °).

C2–C3	1.536 (3)	C8–C9	1.350 (2)
C2–S1	1.8198 (18)	C9–N4	1.373 (2)
C3–N4	1.462 (2)	C9–S1	1.7865 (17)
C5–O4	1.2373 (18)	C12–O5	1.202 (2)
C5–N4	1.375 (2)	C12–O6	1.339 (2)
C5–C6	1.457 (2)	C12–N5	1.378 (2)
C6–C7	1.365 (2)	N5–H5	0.87 (2)
C6–N5	1.394 (2)	O1–S1	1.4864 (13)
C7–C8	1.415 (3)		
C3–C2–S1	111.27 (13)	N4–C9–S1	113.15 (11)
N4–C3–C10	108.75 (12)	O5–C12–O6	126.91 (15)
N4–C3–C2	106.94 (13)	O5–C12–N5	124.90 (15)
C10–C3–C2	110.11 (14)	O6–C12–N5	108.18 (14)
O4–C5–N4	120.76 (14)	C9–N4–C5	123.76 (13)
O4–C5–C6	124.23 (16)	C9–N4–C3	117.54 (13)
N4–C5–C6	115.01 (13)	C5–N4–C3	118.68 (12)
C7–C6–N5	127.08 (15)	C12–N5–C6	126.10 (14)
C7–C6–C5	120.92 (15)	C12–N5–H5	115.8 (14)
N5–C6–C5	111.99 (13)	C6–N5–H5	117.6 (14)
C6–C7–C8	120.41 (15)	O1–S1–C9	107.25 (8)
C9–C8–C7	118.93 (15)	O1–S1–C2	107.93 (9)
C8–C9–N4	120.91 (15)	C9–S1–C2	90.29 (8)
C8–C9–S1	125.81 (13)		

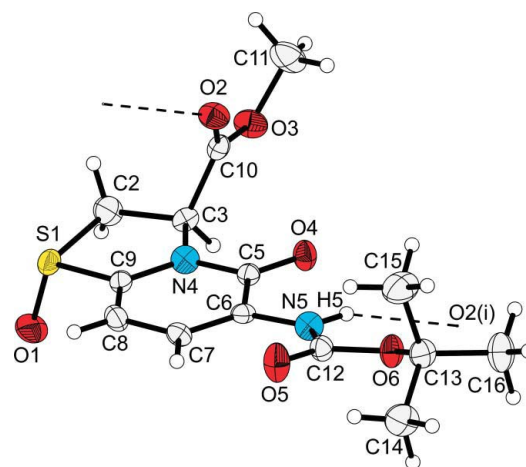


Figure 1

View of (I) (50% probability displacement ellipsoids). Dashed lines indicate N–H···O hydrogen bonds.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N5–H5···O2 ⁱ	0.87 (2)	2.37 (2)	3.1970 (19)	158.4 (18)
C2–H22···O4 ⁱⁱ	0.94 (3)	2.48 (3)	3.387 (3)	162.3 (19)
C3–H3···O1 ⁱⁱⁱ	0.992 (18)	2.535 (17)	3.142 (2)	119.3 (12)
C8–H8···O5 ^{iv}	0.89 (2)	2.47 (2)	3.148 (2)	133.2 (17)
C11–H112···O4 ^v	0.98 (2)	2.45 (2)	3.428 (2)	179 (2)
C11–H113···O3 ^v	1.00 (3)	2.59 (3)	3.095 (3)	111.1 (16)
C16–H163···O2 ^{vi}	0.96 (3)	2.54 (3)	3.427 (2)	153 (2)

Symmetry codes: (i) *x*, 1 + *y*, *z*; (ii) *x*, *y* – 1, *z*; (iii) 1 – *x*, $\frac{1}{2}$ + *y*, 1 – *z*; (iv) 2 – *x*, *y* – $\frac{1}{2}$, 1 – *z*; (v) 1 – *x*, *y* – $\frac{1}{2}$, 2 – *z*; (vi) 2 – *x*, $\frac{3}{2}$ + *y*, 2 – *z*.

All H atoms were located and refined isotropically. The bond-length range for C–H is 0.89 (2)–1.00 (3) Å and the N–H bond length is 0.87 (2) Å. The absolute structure has been determined *via* the refining of an inversion twin.

Data collection: *X-AREA* (Stoe & Cie, 2003); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2004); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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