

(R)-(-)-N-Isovalerylcamphorsultam

Wei Zhou, Shijie Zhang and Weixiao Hu*

College of Pharmaceutical Science, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China

Correspondence e-mail: huyang@mail.hz.zj.cn

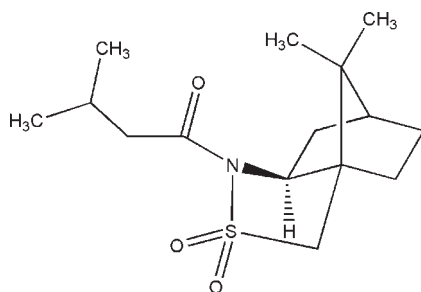
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.045; wR factor = 0.109; data-to-parameter ratio = 17.3.

The title compound, $\text{C}_{15}\text{H}_{25}\text{NO}_3\text{S}$, was prepared from (*R*)-(-)-camphorsultam and isovaleryl chloride. The asymmetric unit contains two independent molecules with slightly different conformations. In the crystal, weak intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds link molecules into two independent hydrogen-bonded chains propagating along the *a* and *b* axes.

Related literature

The title compound is used to obtain a key intermediate in the synthesis of the new renin inhibitor Aliskiren. For the properties of Aliskiren, see Mariano *et al.* (2008).

**Experimental***Crystal data*

$\text{C}_{15}\text{H}_{25}\text{NO}_3\text{S}$
 $M_r = 299.42$
 Tetragonal, $P4_1$

$a = 7.9038$ (7) Å
 $c = 50.228$ (8) Å
 $V = 3137.8$ (7) Å³

$Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 0.21$ mm⁻¹

$T = 293$ K
 $0.30 \times 0.30 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.939$, $T_{\max} = 0.959$
 16320 measured reflections
 6416 independent reflections
 5184 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.109$
 $S = 1.04$
 6416 reflections
 370 parameters
 1 restraint

H-atom parameters constrained
 $\Delta\rho_{\max} = 0.38$ e Å⁻³
 $\Delta\rho_{\min} = -0.19$ e Å⁻³
 Absolute structure: Flack (1983),
 2779 Friedel pairs
 Flack parameter: 0.03 (6)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C4}-\text{H4A}\cdots\text{O3}^i$	0.97	2.45	3.387 (3)	162
$\text{C15}'-\text{H15F}\cdots\text{O3}^{ii}$	0.96	2.49	3.450 (5)	173

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2605).

References

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supplementary materials

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(*R*)-(-)-*N*-Isovalerylcamphorsultam

W. Zhou, S. Zhang and W. Hu

Comment

Aliskiren is a new renin inhibitor, useful for the treatment of hypertension and related cardiovascular diseases (Mariano *et al.*, 2008). In the process of synthesis of Aliskiren, the optically active compound ethyl (2*S*, 4*E*)-5-chloro-2-isopropylpent-4-enoate, (2 in Fig 2), is a key intermediate. In order to obtain the compound (2), we used (*R*)-(-)camphorsultam as a chiral supplementary agent (Fig. 2). Thus, the title compound, (1), was prepared by reacting isovaleryl chloride with (*R*)-(-)camphorsultam.

The molecular structure of (1) is illustrated in Fig. 1. The five-membered ring (C4, C5, C10, N1, S1) shows nearly a C5 β -envelope conformation, with the atom C5 deviating from the plane C4/C10/N1/S1 by 0.459 (4) Å. The plane formed by atom C2, C3, O3 and N1, have a dihedral angle of 19.6 (2)° with the aforementioned plane. In contrast, in the other independent molecule, the five-membered ring (C4', C5', C10', N1', S1') is close to a C10 α -envelope conformation, with the atom C10 deviating from the plane C4'/C5'/N1'/S1' by 0.425 (4) Å. The plane (C2', C3', O3', N1') forms a dihedral angle of 23.9 (2)° with the aforementioned plane. Besides, there exist different bond lengths in the two independent molecules. The bond lengths of C1—C2 (1.508 Å), C1—C11 (1.524 Å) and C1—C12 (1.502 Å) are obviously longer than that of C1'-C2' (1.475 Å), C1'-C11' (1.508 Å) and C1'-C12' (1.476 Å), respectively.

In the crystal packing, there are two different intermolecular hydrogen bonds C—H \cdots O (Table 1). The difference in the intermolecular hydrogen bonding interactions most possibly resulted in their slightly different bond lengths and molecular conformations.

Experimental

In a 250 ml bottomed flask was added camphorsultam (19 g, 88 mmol), toluene (100 ml), anhydrous triethylamine (16 ml, 110 mmol) and 4-dimethylaminopyridine (1.1 g, 10 mmol). The mixture was cooled to 273 K and then 12 ml of isovaleryl chloride were dripped in twenty minutes. After the addition, the mixture was stirred at 298 K until the TLC test showed that the reaction is complete. A solution of 13 ml of 36% hydrochloric acid in 19 ml of water was added at 298 K. The organic layers were separated and the aqueous layer was extracted for three times with 60 ml of dichloromethane. The combined organic layers were washed with water and concentrated to residue under vacuum, obtaining 26.7 g colourless crystal title compound (yield 94%, m.p. 403–406 K). Since the crystal product was not found to be suitable for X-ray diffraction studies, a few crystals were dissolved in toluene, which was allowed to evaporate slowly to give colourless crystals of (1) suitable for X-ray diffraction studies.

Refinement

All H atoms were placed in calculated positions (C—H 0.96–0.98 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}$ of the parent atom.

Figures

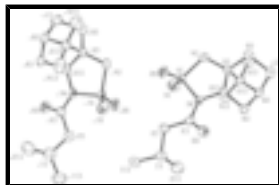


Fig. 1. The content of asymmetric part of (1) showing the atomic numbering and 30% probability displacement ellipsoids. H atoms omitted for clarity.



Fig. 2. Preparation of the title compound.

(R)-(-)-N-Isovalerylcamphorsultam

Crystal data

$C_{15}H_{25}NO_3S$

$M_r = 299.42$

Tetragonal, $P4_1$

Hall symbol: $P\ 4w$

$a = 7.9038\ (7)\ \text{\AA}$

$c = 50.228\ (8)\ \text{\AA}$

$V = 3137.8\ (7)\ \text{\AA}^3$

$Z = 8$

$F(000) = 1296$

$D_x = 1.268\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 25 reflections

$\theta = 12\text{--}18^\circ$

$\mu = 0.21\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Prism, colourless

$0.30 \times 0.30 \times 0.20\ \text{mm}$

Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

φ and ω scans

Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.939$, $T_{\max} = 0.959$

16320 measured reflections

6416 independent reflections

5184 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.035$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.6^\circ$

$h = -10 \rightarrow 5$

$k = -10 \rightarrow 10$

$l = -64 \rightarrow 51$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.109$

$S = 1.04$

6416 reflections

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2 + 0.2775P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.38\ \text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.19\ \text{e \AA}^{-3}$

370 parameters
 1 restraint
 Primary atom site location: structure-invariant direct methods
 Secondary atom site location: difference Fourier map

Extinction correction: *SHELXL97* (Sheldrick, 2008),
 $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0164 (9)
 Absolute structure: Flack (1983), 2779 Friedel pairs
 Flack parameter: 0.03 (6)

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. 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 (Å^2)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
S1	0.78736 (8)	0.43930 (9)	0.123672 (15)	0.04709 (19)
N1	0.9609 (3)	0.3737 (3)	0.14051 (4)	0.0397 (5)
O1	0.7275 (3)	0.5927 (3)	0.13478 (6)	0.0730 (7)
O2	0.8219 (3)	0.4381 (3)	0.09586 (5)	0.0744 (7)
O3	1.2414 (2)	0.3426 (3)	0.14096 (5)	0.0658 (6)
C1	1.3005 (4)	0.6926 (4)	0.13051 (7)	0.0611 (9)
H1	1.3948	0.6184	0.1264	0.073*
C2	1.1411 (3)	0.6024 (4)	0.12208 (7)	0.0560 (8)
H2A	1.0441	0.6718	0.1266	0.067*
H2B	1.1422	0.5881	0.1029	0.067*
C3	1.1225 (3)	0.4323 (4)	0.13503 (6)	0.0458 (7)
C4	0.6596 (3)	0.2646 (4)	0.13288 (6)	0.0463 (7)
H4A	0.5484	0.3030	0.1384	0.056*
H4B	0.6464	0.1879	0.1179	0.056*
C5	0.7480 (3)	0.1757 (3)	0.15582 (5)	0.0393 (6)
C6	0.7286 (4)	-0.0169 (4)	0.15733 (7)	0.0569 (8)
H6A	0.7891	-0.0725	0.1430	0.068*
H6B	0.6105	-0.0501	0.1567	0.068*
C7	0.8086 (5)	-0.0579 (4)	0.18471 (7)	0.0669 (10)
H7A	0.7287	-0.1159	0.1962	0.080*
H7B	0.9090	-0.1275	0.1827	0.080*
C8	0.8533 (4)	0.1164 (4)	0.19581 (6)	0.0542 (7)
H8	0.8647	0.1195	0.2152	0.065*
C9	1.0083 (3)	0.1827 (4)	0.18085 (6)	0.0503 (7)
H9A	1.1005	0.1018	0.1814	0.060*
H9B	1.0466	0.2896	0.1881	0.060*
C10	0.9399 (3)	0.2045 (3)	0.15241 (5)	0.0399 (6)

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H10	0.9879	0.1179	0.1407	0.048*
C11	1.3250 (5)	0.8542 (6)	0.11444 (10)	0.0983 (16)
H11A	1.2336	0.9308	0.1180	0.147*
H11B	1.3266	0.8274	0.0958	0.147*
H11C	1.4302	0.9062	0.1193	0.147*
C12	1.3038 (6)	0.7248 (6)	0.15998 (8)	0.1006 (15)
H12A	1.2079	0.7925	0.1649	0.151*
H12B	1.4060	0.7835	0.1646	0.151*
H12C	1.2996	0.6189	0.1693	0.151*
C13	0.7110 (3)	0.2307 (4)	0.18487 (6)	0.0493 (7)
C14	0.7325 (5)	0.4182 (4)	0.19173 (7)	0.0672 (9)
H14A	0.7242	0.4330	0.2107	0.101*
H14B	0.6455	0.4828	0.1831	0.101*
H14C	0.8413	0.4564	0.1857	0.101*
C15	0.5316 (4)	0.1818 (5)	0.19420 (7)	0.0732 (10)
H15A	0.5200	0.2063	0.2128	0.110*
H15B	0.5137	0.0631	0.1913	0.110*
H15C	0.4494	0.2455	0.1843	0.110*
S1'	0.90760 (10)	0.85718 (10)	0.063320 (15)	0.0537 (2)
N1'	0.8697 (3)	1.0177 (3)	0.04197 (5)	0.0450 (5)
O1'	1.0708 (3)	0.7888 (3)	0.05816 (6)	0.0780 (7)
O2'	0.8725 (4)	0.9123 (3)	0.08967 (5)	0.0811 (7)
O3'	0.8603 (3)	1.2988 (3)	0.03577 (5)	0.0767 (7)
C1'	1.2148 (6)	1.3263 (6)	0.05161 (9)	0.0902 (13)
H1'	1.1589	1.4337	0.0547	0.108*
C2'	1.0962 (5)	1.1959 (5)	0.06127 (8)	0.0748 (10)
H2'1	1.0676	1.2212	0.0796	0.090*
H2'2	1.1537	1.0875	0.0611	0.090*
C3'	0.9354 (4)	1.1795 (4)	0.04570 (7)	0.0557 (7)
C4'	0.7438 (4)	0.7217 (4)	0.05125 (6)	0.0559 (8)
H4'1	0.7895	0.6114	0.0468	0.067*
H4'2	0.6569	0.7072	0.0647	0.067*
C5'	0.6707 (4)	0.8062 (3)	0.02665 (6)	0.0479 (7)
C6'	0.4805 (4)	0.7925 (4)	0.02243 (8)	0.0676 (9)
H6'1	0.4192	0.8602	0.0353	0.081*
H6'2	0.4429	0.6760	0.0237	0.081*
C7'	0.4565 (5)	0.8626 (5)	-0.00620 (8)	0.0786 (11)
H7'1	0.4012	0.7803	-0.0176	0.094*
H7'2	0.3905	0.9661	-0.0061	0.094*
C8'	0.6380 (5)	0.8958 (4)	-0.01530 (7)	0.0626 (9)
H8'	0.6520	0.8977	-0.0347	0.075*
C9'	0.7020 (4)	1.0534 (4)	-0.00152 (6)	0.0580 (8)
H9'1	0.6254	1.1479	-0.0041	0.070*
H9'2	0.8138	1.0845	-0.0078	0.070*
C10'	0.7064 (3)	0.9970 (3)	0.02803 (6)	0.0454 (6)
H10'	0.6164	1.0541	0.0380	0.054*
C11'	1.3725 (5)	1.3300 (7)	0.06852 (10)	0.1022 (15)
H11D	1.3431	1.3603	0.0864	0.153*
H11E	1.4501	1.4119	0.0615	0.153*

H11F	1.4245	1.2203	0.0684	0.153*
C12'	1.2521 (7)	1.3223 (8)	0.02283 (10)	0.126 (2)
H12D	1.3430	1.3991	0.0190	0.188*
H12E	1.1532	1.3554	0.0130	0.188*
H12F	1.2844	1.2098	0.0178	0.188*
C13'	0.7403 (4)	0.7537 (4)	-0.00121 (6)	0.0556 (8)
C14'	0.9302 (5)	0.7688 (5)	-0.00515 (8)	0.0767 (10)
H14D	0.9861	0.6782	0.0040	0.115*
H14E	0.9685	0.8752	0.0018	0.115*
H14F	0.9560	0.7627	-0.0238	0.115*
C15'	0.6873 (6)	0.5750 (4)	-0.00991 (8)	0.0832 (12)
H15D	0.7228	0.5560	-0.0279	0.125*
H15E	0.5666	0.5645	-0.0088	0.125*
H15F	0.7396	0.4930	0.0015	0.125*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0360 (3)	0.0494 (4)	0.0558 (5)	0.0009 (3)	-0.0107 (3)	0.0148 (3)
N1	0.0341 (10)	0.0382 (11)	0.0469 (14)	0.0021 (8)	-0.0063 (9)	0.0072 (9)
O1	0.0484 (12)	0.0460 (12)	0.125 (2)	0.0105 (10)	-0.0056 (12)	0.0090 (12)
O2	0.0679 (14)	0.1078 (19)	0.0475 (15)	-0.0144 (13)	-0.0120 (11)	0.0301 (13)
O3	0.0346 (11)	0.0669 (14)	0.0960 (18)	0.0048 (9)	0.0010 (10)	0.0235 (12)
C1	0.0448 (16)	0.075 (2)	0.064 (2)	-0.0131 (14)	-0.0073 (14)	0.0119 (17)
C2	0.0432 (15)	0.0512 (16)	0.074 (2)	-0.0049 (12)	-0.0088 (15)	0.0164 (15)
C3	0.0339 (13)	0.0546 (16)	0.0490 (18)	0.0021 (11)	-0.0026 (12)	0.0072 (13)
C4	0.0357 (13)	0.0543 (16)	0.0490 (18)	-0.0043 (11)	-0.0108 (11)	0.0051 (13)
C5	0.0333 (12)	0.0438 (14)	0.0410 (16)	-0.0049 (10)	-0.0047 (10)	0.0004 (11)
C6	0.0621 (19)	0.0506 (17)	0.058 (2)	-0.0120 (14)	-0.0044 (15)	0.0027 (14)
C7	0.075 (2)	0.063 (2)	0.062 (2)	-0.0076 (16)	-0.0084 (18)	0.0244 (16)
C8	0.0567 (18)	0.069 (2)	0.0372 (17)	-0.0042 (14)	-0.0091 (13)	0.0158 (14)
C9	0.0427 (15)	0.0565 (17)	0.0517 (19)	0.0021 (12)	-0.0108 (13)	0.0132 (13)
C10	0.0367 (13)	0.0385 (13)	0.0446 (17)	0.0037 (10)	-0.0038 (11)	0.0055 (11)
C11	0.087 (3)	0.096 (3)	0.112 (4)	-0.048 (2)	-0.037 (2)	0.045 (3)
C12	0.130 (4)	0.111 (3)	0.061 (3)	-0.049 (3)	-0.010 (2)	-0.007 (2)
C13	0.0422 (15)	0.0645 (18)	0.0414 (18)	-0.0051 (13)	-0.0004 (12)	0.0017 (13)
C14	0.071 (2)	0.075 (2)	0.056 (2)	0.0015 (16)	0.0089 (17)	-0.0191 (17)
C15	0.0524 (19)	0.106 (3)	0.061 (2)	-0.0076 (18)	0.0063 (16)	0.008 (2)
S1'	0.0649 (5)	0.0533 (4)	0.0429 (4)	0.0029 (3)	-0.0098 (4)	0.0148 (3)
N1'	0.0519 (13)	0.0444 (13)	0.0387 (13)	0.0029 (10)	-0.0057 (10)	0.0107 (10)
O1'	0.0608 (14)	0.0726 (15)	0.101 (2)	0.0171 (12)	-0.0151 (13)	0.0223 (14)
O2'	0.126 (2)	0.0773 (16)	0.0398 (14)	-0.0129 (15)	-0.0058 (13)	0.0089 (12)
O3'	0.112 (2)	0.0461 (12)	0.0723 (17)	0.0019 (12)	-0.0297 (14)	0.0058 (11)
C1'	0.090 (3)	0.103 (3)	0.077 (3)	-0.022 (2)	-0.005 (2)	0.003 (2)
C2'	0.076 (2)	0.080 (2)	0.068 (2)	-0.0153 (19)	-0.0178 (19)	0.016 (2)
C3'	0.067 (2)	0.0531 (18)	0.0474 (19)	0.0002 (15)	-0.0044 (15)	0.0064 (14)
C4'	0.068 (2)	0.0507 (16)	0.049 (2)	-0.0011 (14)	-0.0020 (14)	0.0163 (14)
C5'	0.0565 (17)	0.0448 (15)	0.0424 (17)	0.0019 (12)	-0.0045 (13)	0.0096 (12)

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C6'	0.067 (2)	0.067 (2)	0.069 (2)	-0.0115 (16)	-0.0078 (18)	0.0065 (17)
C7'	0.090 (3)	0.066 (2)	0.079 (3)	0.0008 (19)	-0.038 (2)	0.0051 (19)
C8'	0.094 (3)	0.0547 (18)	0.0389 (18)	0.0014 (16)	-0.0167 (16)	0.0085 (14)
C9'	0.075 (2)	0.0490 (16)	0.050 (2)	0.0049 (14)	-0.0130 (15)	0.0122 (14)
C10'	0.0495 (15)	0.0440 (14)	0.0426 (17)	0.0098 (11)	-0.0004 (12)	0.0035 (12)
C11'	0.071 (3)	0.133 (4)	0.103 (4)	-0.025 (2)	-0.009 (2)	-0.010 (3)
C12'	0.139 (4)	0.168 (5)	0.069 (3)	-0.072 (4)	0.025 (3)	-0.011 (3)
C13'	0.081 (2)	0.0451 (16)	0.0402 (18)	0.0032 (14)	-0.0020 (15)	0.0020 (12)
C14'	0.096 (3)	0.081 (2)	0.053 (2)	0.024 (2)	0.0205 (19)	-0.0012 (18)
C15'	0.128 (3)	0.0493 (19)	0.072 (3)	0.004 (2)	-0.010 (2)	-0.0041 (17)

Geometric parameters (Å, °)

S1—O1	1.416 (2)	S1'—O2'	1.421 (3)
S1—O2	1.423 (2)	S1'—O1'	1.422 (2)
S1—N1	1.693 (2)	S1'—N1'	1.688 (2)
S1—C4	1.772 (3)	S1'—C4'	1.786 (3)
N1—C3	1.386 (3)	N1'—C3'	1.393 (4)
N1—C10	1.475 (3)	N1'—C10'	1.477 (3)
O3—C3	1.214 (3)	O3'—C3'	1.221 (4)
C1—C12	1.502 (5)	C1'—C2'	1.475 (5)
C1—C2	1.508 (4)	C1'—C12'	1.476 (6)
C1—C11	1.524 (5)	C1'—C11'	1.508 (6)
C1—H1	0.9700	C1'—H1'	0.9700
C2—C3	1.501 (4)	C2'—C3'	1.498 (5)
C2—H2A	0.9700	C2'—H2'1	0.9700
C2—H2B	0.9700	C2'—H2'2	0.9700
C4—C5	1.520 (4)	C4'—C5'	1.519 (4)
C4—H4A	0.9700	C4'—H4'1	0.9700
C4—H4B	0.9700	C4'—H4'2	0.9700
C5—C6	1.532 (4)	C5'—C6'	1.522 (4)
C5—C10	1.543 (3)	C5'—C10'	1.536 (4)
C5—C13	1.550 (4)	C5'—C13'	1.560 (4)
C6—C7	1.548 (5)	C6'—C7'	1.553 (5)
C6—H6A	0.9700	C6'—H6'1	0.9700
C6—H6B	0.9700	C6'—H6'2	0.9700
C7—C8	1.528 (5)	C7'—C8'	1.529 (5)
C7—H7A	0.9700	C7'—H7'1	0.9700
C7—H7B	0.9700	C7'—H7'2	0.9700
C8—C9	1.530 (4)	C8'—C9'	1.512 (4)
C8—C13	1.544 (4)	C8'—C13'	1.555 (4)
C8—H8	0.9800	C8'—H8'	0.9800
C9—C10	1.537 (4)	C9'—C10'	1.550 (4)
C9—H9A	0.9700	C9'—H9'1	0.9700
C9—H9B	0.9700	C9'—H9'2	0.9700
C10—H10	0.9800	C10'—H10'	0.9800
C11—H11A	0.9599	C11'—H11D	0.9599
C11—H11B	0.9599	C11'—H11E	0.9599
C11—H11C	0.9599	C11'—H11F	0.9599

C12—H12A	0.9599	C12'—H12D	0.9599
C12—H12B	0.9599	C12'—H12E	0.9599
C12—H12C	0.9599	C12'—H12F	0.9599
C13—C14	1.531 (4)	C13'—C14'	1.519 (5)
C13—C15	1.543 (4)	C13'—C15'	1.536 (4)
C14—H14A	0.9599	C14'—H14D	0.9599
C14—H14B	0.9599	C14'—H14E	0.9599
C14—H14C	0.9599	C14'—H14F	0.9599
C15—H15A	0.9599	C15'—H15D	0.9599
C15—H15B	0.9599	C15'—H15E	0.9599
C15—H15C	0.9599	C15'—H15F	0.9599
O1—S1—O2	117.15 (16)	O2'—S1'—O1'	117.62 (17)
O1—S1—N1	109.64 (13)	O2'—S1'—N1'	109.08 (14)
O2—S1—N1	109.45 (13)	O1'—S1'—N1'	109.31 (14)
O1—S1—C4	111.95 (15)	O2'—S1'—C4'	110.99 (16)
O2—S1—C4	111.11 (14)	O1'—S1'—C4'	111.57 (16)
N1—S1—C4	95.32 (11)	N1'—S1'—C4'	96.10 (12)
C3—N1—C10	119.2 (2)	C3'—N1'—C10'	119.4 (2)
C3—N1—S1	123.05 (18)	C3'—N1'—S1'	122.6 (2)
C10—N1—S1	112.89 (15)	C10'—N1'—S1'	111.92 (17)
C12—C1—C2	111.8 (3)	C2'—C1'—C12'	115.7 (4)
C12—C1—C11	112.2 (3)	C2'—C1'—C11'	110.7 (4)
C2—C1—C11	110.7 (3)	C12'—C1'—C11'	112.8 (4)
C12—C1—H1	107.3	C2'—C1'—H1'	105.6
C2—C1—H1	107.3	C12'—C1'—H1'	105.6
C11—C1—H1	107.3	C11'—C1'—H1'	105.6
C3—C2—C1	112.6 (2)	C1'—C2'—C3'	115.3 (3)
C3—C2—H2A	109.1	C1'—C2'—H2'1	108.4
C1—C2—H2A	109.1	C3'—C2'—H2'1	108.4
C3—C2—H2B	109.1	C1'—C2'—H2'2	108.4
C1—C2—H2B	109.1	C3'—C2'—H2'2	108.4
H2A—C2—H2B	107.8	H2'1—C2'—H2'2	107.5
O3—C3—N1	118.0 (2)	O3'—C3'—N1'	118.2 (3)
O3—C3—C2	123.6 (2)	O3'—C3'—C2'	124.0 (3)
N1—C3—C2	118.4 (2)	N1'—C3'—C2'	117.8 (3)
C5—C4—S1	107.21 (17)	C5'—C4'—S1'	106.76 (19)
C5—C4—H4A	110.3	C5'—C4'—H4'1	110.4
S1—C4—H4A	110.3	S1'—C4'—H4'1	110.4
C5—C4—H4B	110.3	C5'—C4'—H4'2	110.4
S1—C4—H4B	110.3	S1'—C4'—H4'2	110.4
H4A—C4—H4B	108.5	H4'1—C4'—H4'2	108.6
C4—C5—C6	116.8 (2)	C4'—C5'—C6'	117.3 (2)
C4—C5—C10	107.4 (2)	C4'—C5'—C10'	109.0 (2)
C6—C5—C10	104.5 (2)	C6'—C5'—C10'	104.9 (2)
C4—C5—C13	119.8 (2)	C4'—C5'—C13'	118.6 (2)
C6—C5—C13	102.3 (2)	C6'—C5'—C13'	101.8 (3)
C10—C5—C13	104.4 (2)	C10'—C5'—C13'	103.7 (2)
C5—C6—C7	102.2 (2)	C5'—C6'—C7'	103.0 (3)
C5—C6—H6A	111.3	C5'—C6'—H6'1	111.2

supplementary materials

C7—C6—H6A	111.3	C7'—C6'—H6'1	111.2
C5—C6—H6B	111.3	C5'—C6'—H6'2	111.2
C7—C6—H6B	111.3	C7'—C6'—H6'2	111.2
H6A—C6—H6B	109.2	H6'1—C6'—H6'2	109.1
C8—C7—C6	103.3 (2)	C8'—C7'—C6'	102.9 (3)
C8—C7—H7A	111.1	C8'—C7'—H7'1	111.2
C6—C7—H7A	111.1	C6'—C7'—H7'1	111.2
C8—C7—H7B	111.1	C8'—C7'—H7'2	111.2
C6—C7—H7B	111.1	C6'—C7'—H7'2	111.2
H7A—C7—H7B	109.1	H7'1—C7'—H7'2	109.1
C7—C8—C9	108.3 (3)	C9'—C8'—C7'	108.6 (3)
C7—C8—C13	103.3 (2)	C9'—C8'—C13'	102.3 (2)
C9—C8—C13	102.0 (2)	C7'—C8'—C13'	103.2 (3)
C7—C8—H8	114.0	C9'—C8'—H8'	113.9
C9—C8—H8	114.0	C7'—C8'—H8'	113.9
C13—C8—H8	114.0	C13'—C8'—H8'	113.9
C8—C9—C10	102.3 (2)	C8'—C9'—C10'	102.1 (2)
C8—C9—H9A	111.3	C8'—C9'—H9'1	111.4
C10—C9—H9A	111.3	C10'—C9'—H9'1	111.4
C8—C9—H9B	111.3	C8'—C9'—H9'2	111.4
C10—C9—H9B	111.3	C10'—C9'—H9'2	111.4
H9A—C9—H9B	109.2	H9'1—C9'—H9'2	109.2
N1—C10—C9	116.0 (2)	N1'—C10'—C5'	106.9 (2)
N1—C10—C5	106.83 (19)	N1'—C10'—C9'	116.2 (2)
C9—C10—C5	103.1 (2)	C5'—C10'—C9'	103.6 (2)
N1—C10—H10	110.2	N1'—C10'—H10'	109.9
C9—C10—H10	110.2	C5'—C10'—H10'	109.9
C5—C10—H10	110.2	C9'—C10'—H10'	109.9
C1—C11—H11A	109.5	C1'—C11'—H11D	109.5
C1—C11—H11B	109.5	C1'—C11'—H11E	109.5
H11A—C11—H11B	109.5	H11D—C11'—H11E	109.5
C1—C11—H11C	109.5	C1'—C11'—H11F	109.5
H11A—C11—H11C	109.5	H11D—C11'—H11F	109.5
H11B—C11—H11C	109.5	H11E—C11'—H11F	109.5
C1—C12—H12A	109.5	C1'—C12'—H12D	109.5
C1—C12—H12B	109.5	C1'—C12'—H12E	109.5
H12A—C12—H12B	109.5	H12D—C12'—H12E	109.5
C1—C12—H12C	109.5	C1'—C12'—H12F	109.5
H12A—C12—H12C	109.5	H12D—C12'—H12F	109.5
H12B—C12—H12C	109.5	H12E—C12'—H12F	109.5
C14—C13—C15	106.0 (3)	C14'—C13'—C15'	107.7 (3)
C14—C13—C8	113.9 (2)	C14'—C13'—C8'	113.4 (3)
C15—C13—C8	114.5 (3)	C15'—C13'—C8'	113.1 (3)
C14—C13—C5	117.5 (2)	C14'—C13'—C5'	116.4 (3)
C15—C13—C5	112.9 (2)	C15'—C13'—C5'	113.8 (3)
C8—C13—C5	91.9 (2)	C8'—C13'—C5'	91.9 (2)
C13—C14—H14A	109.5	C13'—C14'—H14D	109.5
C13—C14—H14B	109.5	C13'—C14'—H14E	109.5
H14A—C14—H14B	109.5	H14D—C14'—H14E	109.5

C13—C14—H14C	109.5	C13'—C14'—H14F	109.5
H14A—C14—H14C	109.5	H14D—C14'—H14F	109.5
H14B—C14—H14C	109.5	H14E—C14'—H14F	109.5
C13—C15—H15A	109.5	C13'—C15'—H15D	109.5
C13—C15—H15B	109.5	C13'—C15'—H15E	109.5
H15A—C15—H15B	109.5	H15D—C15'—H15E	109.5
C13—C15—H15C	109.5	C13'—C15'—H15F	109.5
H15A—C15—H15C	109.5	H15D—C15'—H15F	109.5
H15B—C15—H15C	109.5	H15E—C15'—H15F	109.5
O1—S1—N1—C3	-84.0 (2)	O2'—S1'—N1'—C3'	50.2 (3)
O2—S1—N1—C3	45.8 (3)	O1'—S1'—N1'—C3'	-79.7 (3)
C4—S1—N1—C3	160.5 (2)	C4'—S1'—N1'—C3'	164.9 (3)
O1—S1—N1—C10	121.1 (2)	O2'—S1'—N1'—C10'	-102.0 (2)
O2—S1—N1—C10	-109.1 (2)	O1'—S1'—N1'—C10'	128.1 (2)
C4—S1—N1—C10	5.5 (2)	C4'—S1'—N1'—C10'	12.7 (2)
C12—C1—C2—C3	-61.0 (4)	C12'—C1'—C2'—C3'	-49.4 (6)
C11—C1—C2—C3	173.1 (3)	C11'—C1'—C2'—C3'	-179.3 (4)
C10—N1—C3—O3	-1.8 (4)	C10'—N1'—C3'—O3'	-4.5 (4)
S1—N1—C3—O3	-155.3 (2)	S1'—N1'—C3'—O3'	-154.8 (3)
C10—N1—C3—C2	178.0 (3)	C10'—N1'—C3'—C2'	176.6 (3)
S1—N1—C3—C2	24.5 (4)	S1'—N1'—C3'—C2'	26.4 (4)
C1—C2—C3—O3	-32.1 (5)	C1'—C2'—C3'—O3'	-36.2 (6)
C1—C2—C3—N1	148.1 (3)	C1'—C2'—C3'—N1'	142.5 (4)
O1—S1—C4—C5	-99.1 (2)	O2'—S1'—C4'—C5'	119.9 (2)
O2—S1—C4—C5	127.8 (2)	O1'—S1'—C4'—C5'	-106.8 (2)
N1—S1—C4—C5	14.6 (2)	N1'—S1'—C4'—C5'	6.7 (2)
S1—C4—C5—C6	-146.5 (2)	S1'—C4'—C5'—C6'	-142.3 (3)
S1—C4—C5—C10	-29.6 (3)	S1'—C4'—C5'—C10'	-23.4 (3)
S1—C4—C5—C13	89.1 (2)	S1'—C4'—C5'—C13'	94.8 (3)
C4—C5—C6—C7	-171.6 (3)	C4'—C5'—C6'—C7'	-170.4 (3)
C10—C5—C6—C7	69.9 (3)	C10'—C5'—C6'—C7'	68.6 (3)
C13—C5—C6—C7	-38.7 (3)	C13'—C5'—C6'—C7'	-39.3 (3)
C5—C6—C7—C8	3.2 (3)	C5'—C6'—C7'—C8'	3.8 (3)
C6—C7—C8—C9	-74.1 (3)	C6'—C7'—C8'—C9'	-74.8 (3)
C6—C7—C8—C13	33.6 (3)	C6'—C7'—C8'—C13'	33.2 (3)
C7—C8—C9—C10	65.4 (3)	C7'—C8'—C9'—C10'	65.7 (3)
C13—C8—C9—C10	-43.2 (3)	C13'—C8'—C9'—C10'	-42.9 (3)
C3—N1—C10—C9	66.2 (3)	C3'—N1'—C10'—C5'	179.0 (3)
S1—N1—C10—C9	-137.8 (2)	S1'—N1'—C10'—C5'	-27.8 (3)
C3—N1—C10—C5	-179.5 (2)	C3'—N1'—C10'—C9'	63.9 (3)
S1—N1—C10—C5	-23.5 (3)	S1'—N1'—C10'—C9'	-142.9 (2)
C8—C9—C10—N1	125.2 (2)	C4'—C5'—C10'—N1'	32.4 (3)
C8—C9—C10—C5	8.9 (3)	C6'—C5'—C10'—N1'	158.8 (2)
C4—C5—C10—N1	33.5 (3)	C13'—C5'—C10'—N1'	-94.8 (3)
C6—C5—C10—N1	158.2 (2)	C4'—C5'—C10'—C9'	155.7 (2)
C13—C5—C10—N1	-94.7 (2)	C6'—C5'—C10'—C9'	-78.0 (3)
C4—C5—C10—C9	156.2 (2)	C13'—C5'—C10'—C9'	28.5 (3)
C6—C5—C10—C9	-79.1 (3)	C8'—C9'—C10'—N1'	125.4 (3)
C13—C5—C10—C9	28.0 (3)	C8'—C9'—C10'—C5'	8.5 (3)

supplementary materials

C7—C8—C13—C14	-176.2 (3)	C9'—C8'—C13'—C14'	-62.0 (4)
C9—C8—C13—C14	-63.8 (3)	C7'—C8'—C13'—C14'	-174.7 (3)
C7—C8—C13—C15	61.5 (3)	C9'—C8'—C13'—C15'	174.9 (3)
C9—C8—C13—C15	173.9 (3)	C7'—C8'—C13'—C15'	62.2 (4)
C7—C8—C13—C5	-54.8 (3)	C9'—C8'—C13'—C5'	57.9 (3)
C9—C8—C13—C5	57.6 (2)	C7'—C8'—C13'—C5'	-54.8 (3)
C4—C5—C13—C14	-53.7 (3)	C4'—C5'—C13'—C14'	-55.3 (4)
C6—C5—C13—C14	175.3 (3)	C6'—C5'—C13'—C14'	174.4 (3)
C10—C5—C13—C14	66.5 (3)	C10'—C5'—C13'—C14'	65.6 (3)
C4—C5—C13—C15	70.3 (3)	C4'—C5'—C13'—C15'	71.0 (4)
C6—C5—C13—C15	-60.8 (3)	C6'—C5'—C13'—C15'	-59.3 (3)
C10—C5—C13—C15	-169.5 (3)	C10'—C5'—C13'—C15'	-168.1 (3)
C4—C5—C13—C8	-172.1 (2)	C4'—C5'—C13'—C8'	-172.7 (3)
C6—C5—C13—C8	56.9 (2)	C6'—C5'—C13'—C8'	57.0 (3)
C10—C5—C13—C8	-51.8 (2)	C10'—C5'—C13'—C8'	-51.7 (3)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C4—H4A \cdots O3 ⁱ	0.97	2.45	3.387 (3)	162
C15'—H15F \cdots O3 ⁱⁱⁱ	0.96	2.49	3.450 (5)	173

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

Fig. 1

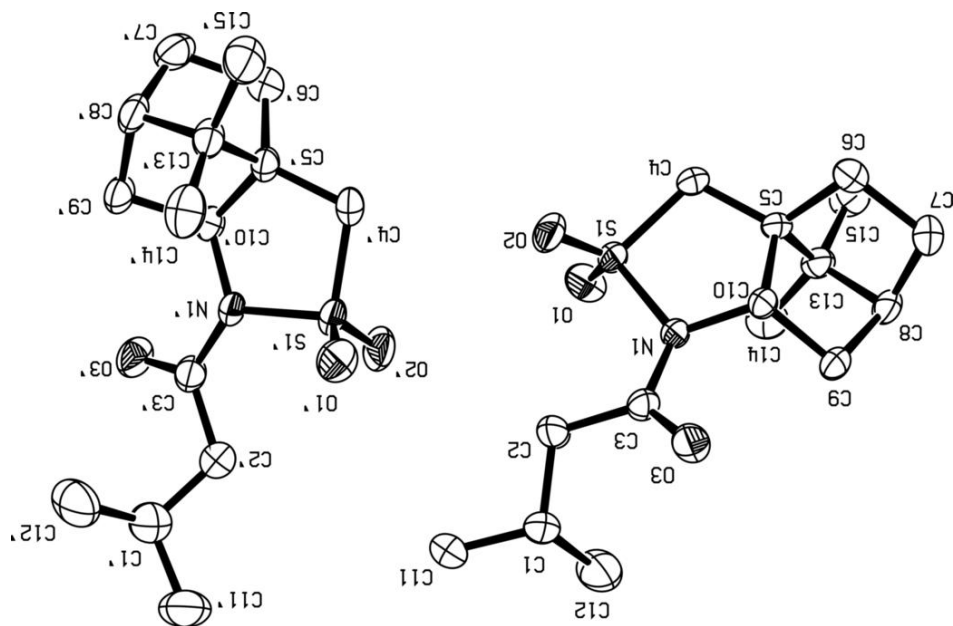


Fig. 2

