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Crystal structure of methyl (2*R*,3*S*)-3-[(*tert*-butylsulfinyl)amino]-2-fluoro-3-phenylpropanoate

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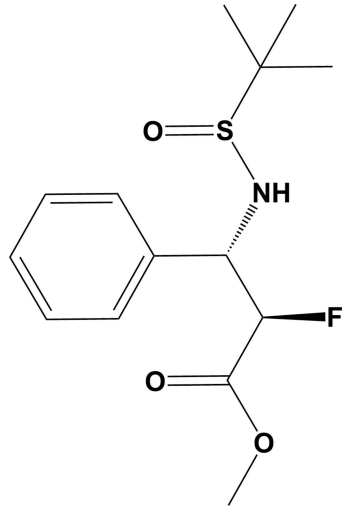
The title compound, $C_{14}H_{20}FNO_3S$, contains two chiral carbon centres and the absolute configuration has been confirmed as (2*R*,3*S*). In the crystal, adjacent molecules are linked by weak C—H···O hydrogen bonds, generating zigzag chains along the *a*-axis direction.

Keywords: crystal structure; fluorine; amino acid; sulfoxide; N—H···O hydrogen bonding.

CCDC reference: 1441329

1. Related literature

For the use of of fluorinated β-amino acids in organic synthesis, see: Marsh (2014); Niemz & Tirrell (2001); Chiu *et al.* (2006). For their synthesis, see: Shang *et al.* (2015); Yoshinari *et al.* (2011); Duggan *et al.* (2010); Peddie & Abell (2012); Jing *et al.* (2011); Pan *et al.* (2010).



2. Experimental

2.1. Crystal data

$C_{14}H_{20}FNO_3S$
M_r = 301.37
Orthorhombic, $P2_12_12_1$
a = 9.1809 (14) Å
b = 9.2384 (15) Å
c = 18.577 (3) Å
V = 1575.7 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.22 mm^{-1}
T = 296 K
0.13 × 0.11 × 0.07 mm

2.2. Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.972, T_{max} = 0.985
8176 measured reflections
2773 independent reflections
2542 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.088
S = 1.04
2773 reflections
186 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}
Absolute structure: Flack (1983)
Absolute structure parameter: 0.05 (8)

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

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14B···O3^{i}	0.96	2.79	3.045 (4)	135

Symmetry code: (i) $x-1, y, z$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXTL*.

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SU5256).

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supporting information

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Crystal structure of methyl (2*R*,3*S*)-3-[(*tert*-butylsulfinyl)amino]-2-fluoro-3-phenylpropanoate

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S1. Synthesis and crystallization

LiHMDS (1.5 ml, 1.0 mol/l in THF) was added to a solution of methyl fluoroacetate (138 mg, 1.5 mmol), (Rs)—N-benzylidene- 2-methylpropane-2-sulfinamide (209 mg, 1.0 mmol), N,N,N′,N′-tetramethyl-ethane-1,2-diamine (0.3 ml), and THF (3 ml) at 203 K. The reaction mixture was stirred for 30 min, then saturated NH_4Cl—H_2O (5 ml) was added, and the quenched reaction mixture was extracted with ethyl acetate (3 × 20 ml). The combined organic layers were dried over anhydrous Na_2SO_4. The obtained compound was recrystallized from ethyl acetate/hexane (1:2) to give colorless crystals.

S1.1. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All the H atoms were placed at calculated positions and treated as riding atoms: N—H = 0.86 Å, C—H = 0.93-0.96 Å with U_{iso}(H) = 1.5U_{eq}(C-methyl and 1.2U_{eq}(N,C) for other H atoms.

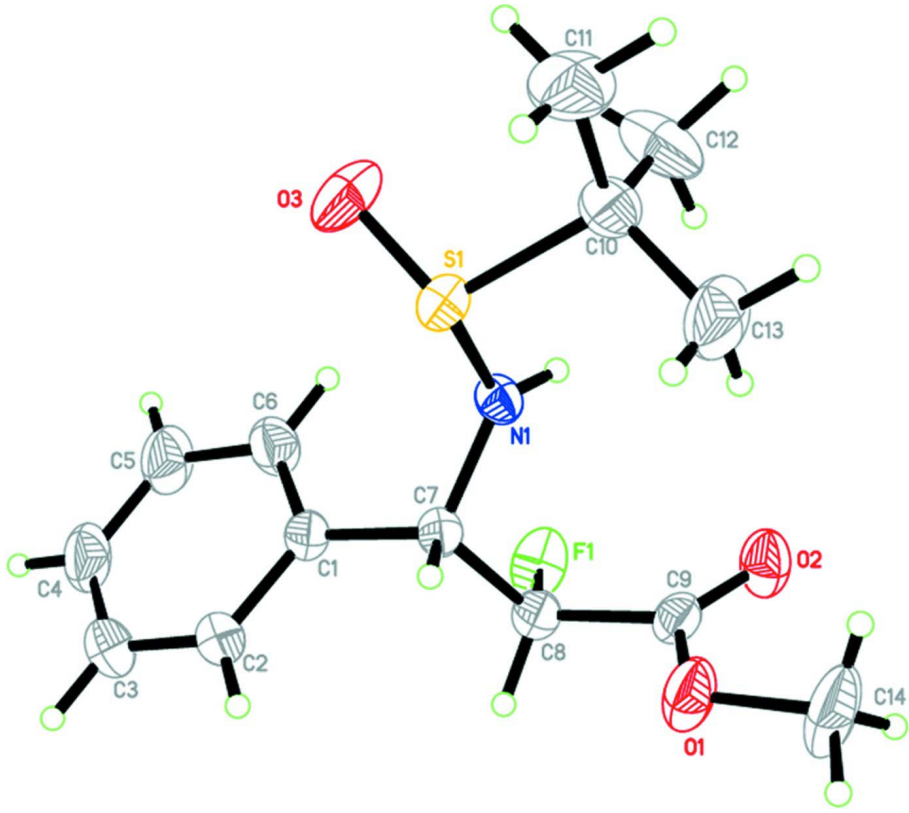

Figure 1

Molecular structure of the title compound, with atom labeling. Displacement ellipsoids are drawn at the 50% probability level.

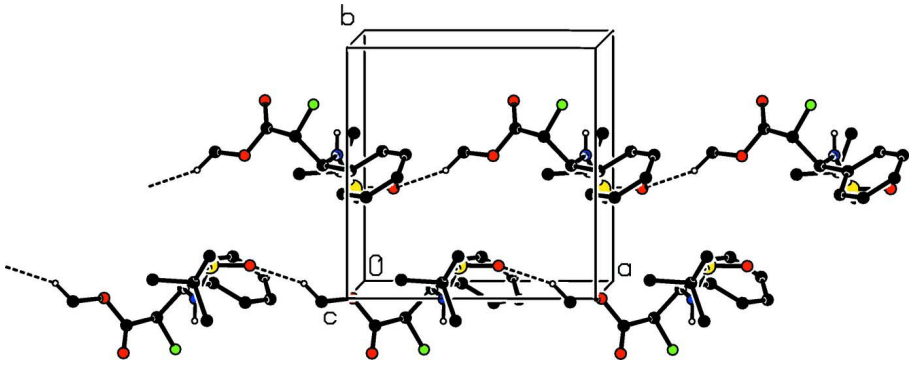

Figure 2

A partial view along the *c* axis of the crystal packing of the title compound. Hydrogen bonds are shown as dashed lines (see Table 1).

Methyl (2*R*,3*S*)-3-[(*tert*-butylsulfinyl)amino]-2-fluoro-3-phenylpropanoate

Crystal data

$C_{14}H_{20}FNO_3S$
M_r = 301.37
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
a = 9.1809 (14) Å
b = 9.2384 (15) Å

c = 18.577 (3) Å
V = 1575.7 (4) Å^3
Z = 4
F(000) = 640
D_x = 1.270 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å

Cell parameters from 3418 reflections
θ = 2.2–25.5°
μ = 0.22 mm^{-1}
T = 296 K
Block, colorless
0.13 × 0.11 × 0.07 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.972, T_{max} = 0.985

8176 measured reflections
2773 independent reflections
2542 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 25.0°, θ_{min} = 2.2°
h = −7→10
k = −11→11
l = −22→21

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.088
S = 1.04
2773 reflections
186 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2 + 0.1714P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0117 (16)
Absolute structure: Flack (1983), **???? Friedel pairs**
Absolute structure parameter: 0.05 (8)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2$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)

	x	y	z	U_{iso}*/U_{eq}
S1	0.45246 (5)	0.13512 (6)	1.04644 (3)	0.04566 (16)
C1	0.4525 (2)	0.0513 (2)	0.86771 (10)	0.0454 (5)
C2	0.4258 (3)	0.1407 (3)	0.80959 (13)	0.0645 (7)
H2	0.3412	0.1960	0.8085	0.077*
C3	0.5233 (3)	0.1489 (4)	0.75313 (14)	0.0799 (8)
H3	0.5032	0.2089	0.7142	0.096*
C4	0.6486 (3)	0.0701 (4)	0.75394 (14)	0.0790 (9)

H4	0.7134	0.0755	0.7156	0.095*
C5	0.6780 (3)	−0.0166 (3)	0.81134 (15)	0.0763 (8)
H5	0.7640	−0.0698	0.8124	0.092*
C6	0.5812 (3)	−0.0262 (3)	0.86807 (13)	0.0614 (6)
H6	0.6029	−0.0855	0.9070	0.074*
C7	0.3370 (2)	0.0338 (2)	0.92539 (10)	0.0412 (4)
H7	0.2837	0.1254	0.9288	0.049*
C8	0.2285 (2)	−0.0833 (2)	0.90203 (11)	0.0485 (5)
H8	0.1834	−0.0536	0.8566	0.058*
C9	0.1100 (2)	−0.1116 (2)	0.95639 (13)	0.0467 (5)
C10	0.3929 (3)	0.0729 (3)	1.13521 (12)	0.0606 (6)
C11	0.4604 (4)	0.1814 (4)	1.18744 (15)	0.0919 (10)
H11A	0.4255	0.1626	1.2352	0.138*
H11B	0.4337	0.2778	1.1734	0.138*
H11C	0.5646	0.1720	1.1865	0.138*
C12	0.4469 (5)	−0.0790 (3)	1.15008 (15)	0.1004 (11)
H12A	0.5481	−0.0858	1.1376	0.151*
H12B	0.3920	−0.1468	1.1218	0.151*
H12C	0.4347	−0.1008	1.2002	0.151*
C13	0.2279 (3)	0.0833 (4)	1.13551 (16)	0.0914 (10)
H13A	0.1880	0.0102	1.1045	0.137*
H13B	0.1989	0.1772	1.1186	0.137*
H13C	0.1924	0.0692	1.1836	0.137*
C14	−0.1016 (3)	−0.0130 (4)	1.00859 (19)	0.0961 (11)
H14A	−0.1445	−0.1076	1.0052	0.144*
H14B	−0.1733	0.0589	0.9969	0.144*
H14C	−0.0670	0.0026	1.0567	0.144*
F1	0.30213 (17)	−0.21153 (14)	0.89103 (8)	0.0696 (4)
N1	0.38966 (18)	−0.00242 (17)	0.99719 (8)	0.0410 (4)
H1	0.3884	−0.0897	1.0133	0.049*
O1	0.02014 (16)	−0.00250 (18)	0.95826 (11)	0.0748 (5)
O2	0.10015 (19)	−0.21952 (17)	0.99189 (10)	0.0648 (5)
O3	0.61290 (18)	0.1341 (2)	1.04867 (11)	0.0792 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0395 (3)	0.0456 (3)	0.0519 (3)	−0.0028 (2)	0.0025 (2)	−0.0062 (2)
C1	0.0440 (11)	0.0485 (11)	0.0438 (11)	−0.0090 (10)	0.0010 (10)	0.0042 (9)
C2	0.0517 (14)	0.0817 (17)	0.0600 (14)	−0.0088 (13)	−0.0025 (11)	0.0254 (13)
C3	0.0740 (19)	0.111 (2)	0.0545 (14)	−0.0187 (18)	0.0034 (13)	0.0315 (15)
C4	0.0731 (19)	0.101 (2)	0.0632 (17)	−0.0250 (17)	0.0232 (15)	0.0080 (16)
C5	0.0572 (15)	0.0885 (19)	0.0832 (18)	0.0025 (15)	0.0285 (13)	0.0076 (16)
C6	0.0578 (14)	0.0670 (14)	0.0595 (14)	0.0055 (12)	0.0115 (11)	0.0130 (12)
C7	0.0402 (10)	0.0416 (10)	0.0418 (10)	−0.0018 (8)	0.0021 (8)	0.0043 (9)
C8	0.0455 (12)	0.0540 (12)	0.0458 (11)	−0.0051 (10)	0.0000 (9)	0.0011 (10)
C9	0.0369 (10)	0.0445 (11)	0.0588 (12)	−0.0058 (8)	−0.0021 (10)	0.0024 (11)
C10	0.0636 (15)	0.0741 (16)	0.0440 (12)	−0.0009 (13)	0.0036 (11)	−0.0078 (11)

C11	0.094 (2)	0.121 (2)	0.0608 (16)	−0.006 (2)	−0.0073 (16)	−0.0322 (16)
C12	0.152 (3)	0.089 (2)	0.0602 (16)	0.007 (2)	−0.020 (2)	0.0179 (15)
C13	0.0664 (18)	0.133 (3)	0.0744 (18)	−0.0155 (18)	0.0280 (15)	−0.0240 (18)
C14	0.0490 (15)	0.0811 (18)	0.158 (3)	0.0062 (14)	0.0448 (19)	0.019 (2)
F1	0.0689 (9)	0.0569 (8)	0.0828 (10)	−0.0086 (7)	0.0215 (7)	−0.0240 (7)
N1	0.0477 (10)	0.0368 (8)	0.0385 (8)	−0.0010 (7)	0.0006 (7)	0.0035 (7)
O1	0.0440 (9)	0.0610 (10)	0.1193 (15)	0.0081 (8)	0.0214 (10)	0.0283 (10)
O2	0.0621 (10)	0.0489 (9)	0.0835 (12)	−0.0020 (7)	0.0163 (9)	0.0133 (9)
O3	0.0401 (8)	0.0993 (14)	0.0981 (13)	−0.0126 (9)	0.0054 (9)	−0.0301 (12)

Geometric parameters (Å, º)

S1—O3	1.4737 (17)	C8—H8	0.9800
S1—N1	1.6685 (17)	C9—O2	1.199 (2)
S1—C10	1.830 (2)	C9—O1	1.303 (3)
C1—C2	1.381 (3)	C10—C12	1.513 (4)
C1—C6	1.381 (3)	C10—C13	1.518 (4)
C1—C7	1.516 (3)	C10—C11	1.527 (4)
C2—C3	1.381 (4)	C11—H11A	0.9600
C2—H2	0.9300	C11—H11B	0.9600
C3—C4	1.361 (4)	C11—H11C	0.9600
C3—H3	0.9300	C12—H12A	0.9600
C4—C5	1.361 (4)	C12—H12B	0.9600
C4—H4	0.9300	C12—H12C	0.9600
C5—C6	1.382 (3)	C13—H13A	0.9600
C5—H5	0.9300	C13—H13B	0.9600
C6—H6	0.9300	C13—H13C	0.9600
C7—N1	1.458 (2)	C14—O1	1.460 (3)
C7—C8	1.533 (3)	C14—H14A	0.9600
C7—H7	0.9800	C14—H14B	0.9600
C8—F1	1.379 (3)	C14—H14C	0.9600
C8—C9	1.507 (3)	N1—H1	0.8600
O3—S1—N1	110.87 (10)	O1—C9—C8	109.95 (18)
O3—S1—C10	105.74 (12)	C12—C10—C13	112.7 (3)
N1—S1—C10	98.71 (10)	C12—C10—C11	111.1 (2)
C2—C1—C6	117.7 (2)	C13—C10—C11	111.2 (2)
C2—C1—C7	119.5 (2)	C12—C10—S1	111.0 (2)
C6—C1—C7	122.66 (17)	C13—C10—S1	106.35 (19)
C1—C2—C3	120.8 (3)	C11—C10—S1	104.17 (19)
C1—C2—H2	119.6	C10—C11—H11A	109.5
C3—C2—H2	119.6	C10—C11—H11B	109.5
C4—C3—C2	120.6 (3)	H11A—C11—H11B	109.5
C4—C3—H3	119.7	C10—C11—H11C	109.5
C2—C3—H3	119.7	H11A—C11—H11C	109.5
C3—C4—C5	119.4 (2)	H11B—C11—H11C	109.5
C3—C4—H4	120.3	C10—C12—H12A	109.5
C5—C4—H4	120.3	C10—C12—H12B	109.5

C4—C5—C6	120.5 (3)	H12A—C12—H12B	109.5
C4—C5—H5	119.8	C10—C12—H12C	109.5
C6—C5—H5	119.8	H12A—C12—H12C	109.5
C1—C6—C5	120.9 (2)	H12B—C12—H12C	109.5
C1—C6—H6	119.5	C10—C13—H13A	109.5
C5—C6—H6	119.5	C10—C13—H13B	109.5
N1—C7—C1	116.05 (17)	H13A—C13—H13B	109.5
N1—C7—C8	108.22 (16)	C10—C13—H13C	109.5
C1—C7—C8	109.24 (16)	H13A—C13—H13C	109.5
N1—C7—H7	107.7	H13B—C13—H13C	109.5
C1—C7—H7	107.7	O1—C14—H14A	109.5
C8—C7—H7	107.7	O1—C14—H14B	109.5
F1—C8—C9	107.71 (16)	H14A—C14—H14B	109.5
F1—C8—C7	109.26 (18)	O1—C14—H14C	109.5
C9—C8—C7	113.67 (17)	H14A—C14—H14C	109.5
F1—C8—H8	108.7	H14B—C14—H14C	109.5
C9—C8—H8	108.7	C7—N1—S1	116.21 (12)
C7—C8—H8	108.7	C7—N1—H1	121.9
O2—C9—O1	125.5 (2)	S1—N1—H1	121.9
O2—C9—C8	124.6 (2)	C9—O1—C14	116.76 (19)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14*B*···O3^{i}	0.96	2.79	3.045 (4)	135

Symmetry code: (i) $x-1, y, z$.