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(*S*)-1-Methyl-2-[1-(*p*-tolylsulfonyl)-pyrrolidin-2-ylmethylsulfanyl]-1*H*-imidazole

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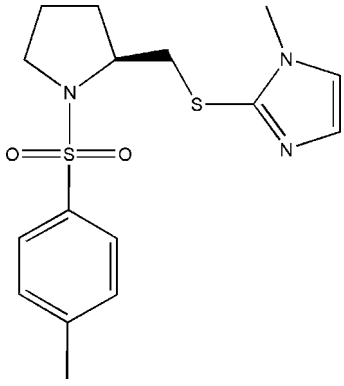
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.007 Å; R factor = 0.072; wR factor = 0.144; data-to-parameter ratio = 14.3.

The title compound, $C_{16}H_{21}N_3O_2S_2$, was synthesized from L-proline. The imidazole and toluene groups are positioned on opposite sides of the pyrrolidine ring. The absolute configuration of the chiral C atom is been determined as *S*. Weak C—H···O and C—H···π interactions stabilize the packing.

Related literature

For related literature, see: Wang *et al.* (2007); Xu *et al.* (2006)



Experimental

Crystal data

$C_{16}H_{21}N_3O_2S_2$
M_r = 351.48
Orthorhombic, $P2_12_12_1$
a = 6.0881 (5) Å
b = 14.7605 (11) Å
c = 18.9354 (14) Å
V = 1701.6 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.33 mm^{-1}
T = 298 (2) K
0.39 × 0.10 × 0.09 mm

Data collection

Bruker APEX area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.884, T_{max} = 0.971
8975 measured reflections
3000 independent reflections
2783 reflections with $I > 2\sigma(I)$
R_{int} = 0.043

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.072
$wR(F^2)$ = 0.144
S = 1.27
3000 reflections
210 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Absolute structure: Flack (1983), with 1244 Friedel pairs
Flack parameter: −0.04 (15)

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

*Cg*1 is the centroid of the imidazole ring.

D—H···A	D—H	H···A	D···A	D—H···A
C15—H15···O2^{i}	0.93	2.49	3.365 (6)	157
C4—H4···O1^{ii}	0.93	2.69	3.425 (6)	137
C16—H16*B*···*Cg*1^{iii}	0.96	2.77	3.643 (5)	152

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (ii) $x-1, y, z$; (iii) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2002); 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: DN2234).

References

Bruker (2002). *SADABS* (Version 2.03), *SAINT* (Version 6.02), *SMART* (Version 5.62) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
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Xu, D. Q., Luo, S. P., Yue, H. D., Wang, L. P., Liu, Y. K. & Xu, Z. Y. (2006). *Synlett*, **16**, 2569–2572.

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supplementary materials

Acta Cryst. (2007). E**63**, o4260 [**doi:10.1107/S1600536807047757**]

(*S*)-1-Methyl-2-[1-(*p*-tolylsulfonyl)pyrrolidin-2-ylmethylsulfanyl]-1*H*-imidazole

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Comment

The (*S*)-1-Methyl-2-(pyrrolidin-2-ylsulfanyl)-1*H*-imidazole is a new structural class of organocatalysts that derive from *L*-proline. By using the toluenesulfonyl to protect the NH group of the pyrrolidine the title compound could be synthesized

The pyrrolidine ring assumed a twisted envelope-like conformation that was similar to other reported *L*-proline derivative compounds (Wang *et al.*, 2007). The absolute configuration of the chiral C11 atom has been determined to be S from the refinement of the Flack parameter (Flack, 1983). The Imidazole and the toluene groups are located on each side of the pyrrolidine ring (Fig. 1).

The occurrence of weak C—H···O hydrogen bonds and C—H···π interactions stabilize the structure (Table 1) (Fig. 2).

Experimental

The title compound was readily synthesized by treating toluenesulfonyl Choilde (11 mmol), $NaCO_3$ (30 mmol) with (*S*)-1-Methyl-2-(pyrrolidin-2-ylsulfanyl)-1*H*-imidazole (10 mmol)in $CHCl_3$ (30 ml) with stirring at room teperature for 24 h with the yield of 95%. (*S*)-1-Methyl-2-(pyrrolidin-2-ylsulfanyl)-1*H*-imidazole was obtained from commercially available *L*-proline by reduction with $NaBH_4$—I_2, a bromination step with PBr_3 and thioether step with mercaptoimidazole successively (Xu *et al.*,2006). Suitable crystals were obtained by slow evaporation of ethanol at room temperature.

Refinement

All H atoms attached were fixed geometrically and treated as riding on their parent atoms with C—H = 0.93 Å (aromatic), 0.96Å (Methyl), 0.97 Å (methylene) and 0.98 Å (methine) with $U_{iso}(H) = 1.2U_{eq}(C)$ or $U_{iso}(H) = 1.5U_{eq}(C_{methyl})$.

Figures

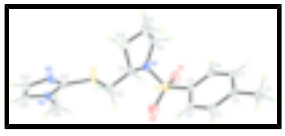

Fig. 1. Molecular view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as small spheres of arbitrary radii.

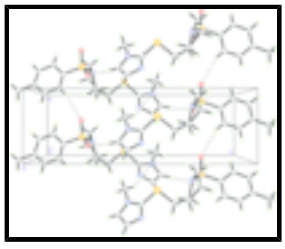

Fig. 2. A packing view of (I). Hydrogen bonds are illustrated as dashed lines.

(*S*)-1-Methyl-2-[1-(*p*-tolylsulfonyl)pyrrolidin-2-ylmethylsulfanyl]-\ 1*H*-imidazole

Crystal data

$C_{16}H_{21}N_3O_2S_2$	F_{000} = 744
M_r = 351.48	D_x = 1.372 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2ac 2ab	Cell parameters from 2004 reflections
a = 6.0881 (5) Å	θ = 2.9–24.8º
b = 14.7605 (11) Å	μ = 0.33 mm^{-1}
c = 18.9354 (14) Å	T = 298 (2) K
V = 1701.6 (2) Å^3	Block, colorless
Z = 4	0.39 × 0.10 × 0.09 mm

Data collection

Bruker APEX area-detector diffractometer	3000 independent reflections
Radiation source: fine-focus sealed tube	2783 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.043
T = 298(2) K	θ_{max} = 25.0º
φ and ω scans	θ_{min} = 1.8º
Absorption correction: multi-scan (SADABS; Bruker, 2002)	h = −7→6
T_{min} = 0.884, T_{max} = 0.971	k = −17→17
8975 measured reflections	l = −9→22

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.072	$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 0.83P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.144	$(\Delta/\sigma)_{max}$ = 0.018
S = 1.27	$\Delta\rho_{max}$ = 0.35 e Å^{-3}
3000 reflections	$\Delta\rho_{min}$ = −0.24 e Å^{-3}
210 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 1244 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: −0.04 (15)

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 $F^2 > 2\mathrm{sigma}(F^2)$ 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	0.3383 (2)	0.67096 (9)	0.23080 (6)	0.0437 (3)
S2	0.1308 (2)	0.60811 (10)	0.42437 (6)	0.0475 (4)
O1	0.5722 (6)	0.6738 (3)	0.22838 (19)	0.0664 (11)
O2	0.2198 (7)	0.7429 (2)	0.2626 (2)	0.0617 (11)
N1	0.2711 (6)	0.5796 (3)	0.2731 (2)	0.0404 (10)
N2	−0.2291 (7)	0.5450 (3)	0.4949 (2)	0.0502 (12)
N3	−0.0441 (7)	0.6493 (2)	0.55296 (19)	0.0362 (9)
C1	0.0066 (9)	0.6334 (4)	−0.0688 (3)	0.0549 (15)
H1A	−0.1437	0.6528	−0.0708	0.082*
H1B	0.0165	0.5713	−0.0836	0.082*
H1C	0.0941	0.6705	−0.0995	0.082*
C2	0.0896 (8)	0.6419 (3)	0.0057 (2)	0.0360 (11)
C3	−0.0376 (8)	0.6812 (3)	0.0575 (3)	0.0399 (12)
H3	−0.1769	0.7022	0.0457	0.048*
C4	0.0342 (8)	0.6904 (3)	0.1260 (2)	0.0381 (11)
H4	−0.0551	0.7171	0.1600	0.046*
C5	0.2426 (7)	0.6592 (3)	0.1435 (2)	0.0324 (10)
C6	0.3746 (8)	0.6195 (3)	0.0924 (2)	0.0382 (11)
H6	0.5138	0.5982	0.1039	0.046*
C7	0.2972 (8)	0.6121 (3)	0.0246 (2)	0.0373 (11)
H7	0.3868	0.5863	−0.0097	0.045*
C8	0.3901 (9)	0.4944 (4)	0.2558 (3)	0.0536 (14)
H8A	0.4879	0.4773	0.2939	0.064*
H8B	0.4753	0.5014	0.2128	0.064*
C9	0.2129 (9)	0.4248 (4)	0.2460 (3)	0.0650 (17)
H9A	0.2645	0.3649	0.2591	0.078*
H9B	0.1621	0.4234	0.1975	0.078*
C10	0.0331 (10)	0.4565 (4)	0.2952 (3)	0.0564 (15)
H10A	0.0646	0.4392	0.3436	0.068*
H10B	−0.1078	0.4312	0.2816	0.068*
C11	0.0335 (8)	0.5598 (3)	0.2870 (2)	0.0409 (12)
H11	−0.0520	0.5760	0.2450	0.049*
C12	−0.0543 (9)	0.6107 (4)	0.3486 (2)	0.0488 (13)
H12A	−0.1945	0.5848	0.3623	0.059*
H12B	−0.0794	0.6731	0.3350	0.059*
C13	−0.0626 (8)	0.5992 (3)	0.4934 (2)	0.0381 (11)
C14	−0.3253 (9)	0.5614 (3)	0.5584 (3)	0.0528 (14)
H14	−0.4523	0.5330	0.5743	0.063*

C15	−0.2137 (8)	0.6236 (3)	0.5949 (3)	0.0438 (12)
H15	−0.2457	0.6449	0.6400	0.053*
C16	0.1183 (9)	0.7187 (4)	0.5690 (3)	0.0563 (14)
H16A	0.0685	0.7544	0.6082	0.084*
H16B	0.1381	0.7570	0.5286	0.084*
H16C	0.2554	0.6904	0.5808	0.084*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0450 (7)	0.0534 (8)	0.0329 (6)	−0.0060 (6)	−0.0042 (6)	−0.0057 (6)
S2	0.0395 (7)	0.0676 (9)	0.0352 (7)	−0.0031 (6)	0.0066 (6)	−0.0066 (7)
O1	0.051 (2)	0.091 (3)	0.058 (2)	−0.023 (2)	−0.0102 (19)	0.005 (2)
O2	0.088 (3)	0.050 (2)	0.047 (2)	−0.005 (2)	0.000 (2)	−0.0157 (18)
N1	0.039 (2)	0.057 (3)	0.025 (2)	0.0085 (19)	−0.0006 (17)	−0.0016 (19)
N2	0.055 (3)	0.041 (2)	0.054 (3)	−0.014 (2)	0.017 (2)	−0.019 (2)
N3	0.046 (2)	0.034 (2)	0.029 (2)	−0.0044 (18)	−0.0004 (18)	−0.0055 (17)
C1	0.070 (4)	0.053 (3)	0.041 (3)	−0.007 (3)	−0.012 (3)	0.008 (3)
C2	0.049 (3)	0.025 (2)	0.034 (2)	−0.008 (2)	−0.001 (2)	0.008 (2)
C3	0.035 (2)	0.036 (3)	0.049 (3)	0.003 (2)	0.000 (2)	0.014 (2)
C4	0.043 (3)	0.038 (3)	0.033 (3)	0.007 (2)	0.010 (2)	0.007 (2)
C5	0.041 (3)	0.029 (2)	0.028 (2)	−0.002 (2)	0.004 (2)	0.008 (2)
C6	0.037 (2)	0.041 (3)	0.036 (3)	0.002 (2)	0.003 (2)	0.002 (2)
C7	0.048 (3)	0.034 (3)	0.030 (2)	0.005 (2)	0.008 (2)	−0.001 (2)
C8	0.050 (3)	0.073 (4)	0.037 (3)	0.024 (3)	0.011 (3)	0.013 (3)
C9	0.070 (4)	0.067 (4)	0.058 (4)	0.016 (3)	−0.008 (3)	−0.010 (3)
C10	0.054 (3)	0.057 (3)	0.059 (3)	−0.004 (3)	−0.006 (3)	−0.009 (3)
C11	0.035 (2)	0.059 (3)	0.028 (3)	0.008 (2)	0.000 (2)	0.004 (2)
C12	0.048 (3)	0.062 (3)	0.037 (3)	0.011 (3)	−0.002 (2)	−0.001 (3)
C13	0.043 (3)	0.033 (2)	0.038 (3)	0.005 (2)	0.003 (2)	0.002 (2)
C14	0.056 (3)	0.042 (3)	0.060 (3)	−0.013 (3)	0.029 (3)	−0.011 (3)
C15	0.058 (3)	0.041 (3)	0.033 (3)	0.003 (2)	0.014 (2)	−0.004 (2)
C16	0.057 (3)	0.058 (3)	0.054 (3)	−0.003 (3)	−0.005 (3)	−0.013 (3)

Geometric parameters (Å, °)

S1—O2	1.418 (4)	C5—C6	1.388 (6)
S1—O1	1.425 (4)	C6—C7	1.372 (6)
S1—N1	1.621 (4)	C6—H6	0.9300
S1—C5	1.761 (4)	C7—H7	0.9300
S2—C13	1.765 (5)	C8—C9	1.501 (8)
S2—C12	1.824 (5)	C8—H8A	0.9700
N1—C8	1.488 (6)	C8—H8B	0.9700
N1—C11	1.499 (6)	C9—C10	1.512 (7)
N2—C13	1.292 (6)	C9—H9A	0.9700
N2—C14	1.358 (6)	C9—H9B	0.9700
N3—C13	1.353 (6)	C10—C11	1.533 (7)
N3—C15	1.357 (6)	C10—H10A	0.9700
N3—C16	1.455 (6)	C10—H10B	0.9700

C1—C2	1.503 (7)	C11—C12	1.487 (6)
C1—H1A	0.9600	C11—H11	0.9800
C1—H1B	0.9600	C12—H12A	0.9700
C1—H1C	0.9600	C12—H12B	0.9700
C2—C3	1.378 (6)	C14—C15	1.336 (7)
C2—C7	1.386 (6)	C14—H14	0.9300
C3—C4	1.377 (7)	C15—H15	0.9300
C3—H3	0.9300	C16—H16A	0.9600
C4—C5	1.390 (6)	C16—H16B	0.9600
C4—H4	0.9300	C16—H16C	0.9600
O2—S1—O1	120.0 (3)	C9—C8—H8B	110.8
O2—S1—N1	106.6 (2)	H8A—C8—H8B	108.9
O1—S1—N1	107.0 (2)	C8—C9—C10	103.5 (4)
O2—S1—C5	107.7 (2)	C8—C9—H9A	111.1
O1—S1—C5	107.6 (2)	C10—C9—H9A	111.1
N1—S1—C5	107.3 (2)	C8—C9—H9B	111.1
C13—S2—C12	99.9 (2)	C10—C9—H9B	111.1
C8—N1—C11	110.1 (4)	H9A—C9—H9B	109.0
C8—N1—S1	118.1 (3)	C9—C10—C11	104.1 (5)
C11—N1—S1	119.5 (3)	C9—C10—H10A	110.9
C13—N2—C14	104.3 (4)	C11—C10—H10A	110.9
C13—N3—C15	105.8 (4)	C9—C10—H10B	110.9
C13—N3—C16	128.0 (4)	C11—C10—H10B	110.9
C15—N3—C16	126.2 (4)	H10A—C10—H10B	108.9
C2—C1—H1A	109.5	C12—C11—N1	112.8 (4)
C2—C1—H1B	109.5	C12—C11—C10	114.9 (4)
H1A—C1—H1B	109.5	N1—C11—C10	102.3 (4)
C2—C1—H1C	109.5	C12—C11—H11	108.9
H1A—C1—H1C	109.5	N1—C11—H11	108.9
H1B—C1—H1C	109.5	C10—C11—H11	108.9
C3—C2—C7	117.5 (4)	C11—C12—S2	112.6 (4)
C3—C2—C1	121.0 (4)	C11—C12—H12A	109.1
C7—C2—C1	121.5 (4)	S2—C12—H12A	109.1
C4—C3—C2	122.3 (4)	C11—C12—H12B	109.1
C4—C3—H3	118.8	S2—C12—H12B	109.1
C2—C3—H3	118.8	H12A—C12—H12B	107.8
C3—C4—C5	118.8 (4)	N2—C13—N3	112.7 (4)
C3—C4—H4	120.6	N2—C13—S2	125.9 (4)
C5—C4—H4	120.6	N3—C13—S2	121.4 (4)
C6—C5—C4	120.1 (4)	C15—C14—N2	111.2 (5)
C6—C5—S1	120.3 (3)	C15—C14—H14	124.4
C4—C5—S1	119.5 (3)	N2—C14—H14	124.4
C7—C6—C5	119.2 (4)	C14—C15—N3	106.0 (4)
C7—C6—H6	120.4	C14—C15—H15	127.0
C5—C6—H6	120.4	N3—C15—H15	127.0
C6—C7—C2	122.0 (4)	N3—C16—H16A	109.5
C6—C7—H7	119.0	N3—C16—H16B	109.5
C2—C7—H7	119.0	H16A—C16—H16B	109.5
N1—C8—C9	104.8 (4)	N3—C16—H16C	109.5

N1—C8—H8A	110.8	H16A—C16—H16C	109.5
C9—C8—H8A	110.8	H16B—C16—H16C	109.5
N1—C8—H8B	110.8		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15···O2^{i}	0.93	2.49	3.365 (6)	157
C4—H4···O1^{ii}	0.93	2.69	3.425 (6)	137
C16—H16B···Cg1^{iii}	0.96	2.77	3.643 (5)	152

Symmetry codes: (i) *x*−1/2, −*y*+3/2, −*z*+1; (ii) *x*−1, *y*, *z*; (iii) *x*+1/2, −*y*+3/2, −*z*+1.

Fig. 1

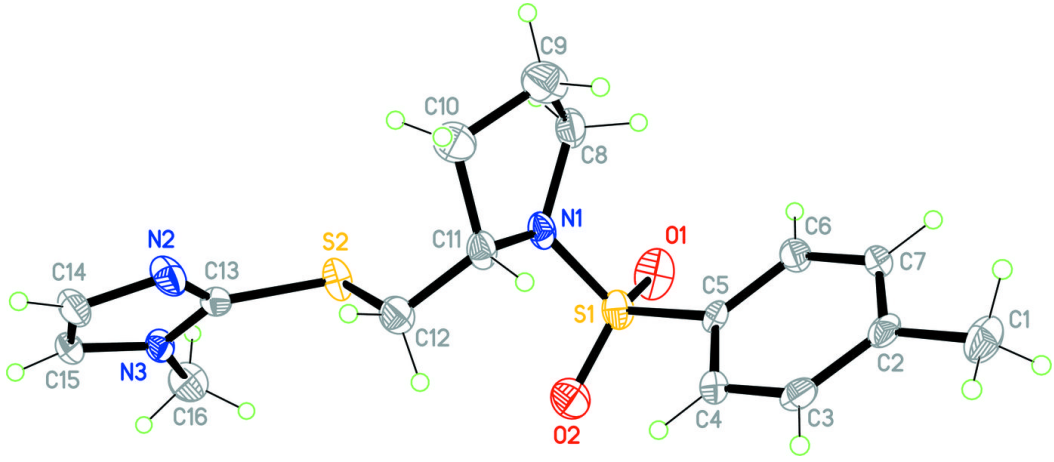
C9
C10
C8
N1
O1
C11
S2
N2
C13
C14
C6
C7
C5
S1
C12
C1
C15
N3
C16
C2
C4
C3
O2

Fig. 2