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(*S*)-2-(Iodomethyl)-1-tosylpyrrolidine

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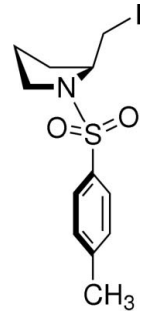
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.009 Å; R factor = 0.037; wR factor = 0.092; data-to-parameter ratio = 15.5.

In the title molecule, $C_{12}H_{16}INO_2S$, the pyrrolidine ring is in an envelope conformation. The dihedral angle between the four essentially coplanar atoms of the pyrrolidine ring and the benzene ring is 75.5 (4)°.

Related literature

For leading reviews, see: Allemann *et al.* (2004); List (2004); Notz *et al.* (2004); For related literature, see: Bahmanyar *et al.* (2003); List *et al.* (2000); Northrup & MacMillan, (2002); Sakthivel *et al.* (2001); Barbas *et al.* (1997); Dalko & Moisan (2004); Eder *et al.* (1971); Hajos & Parrish (1974); Machajewski & Wong (2000); Seayed & List (2005); Wagner *et al.* (1995).



Experimental

Crystal data

$C_{12}H_{16}INO_2S$
M_r = 365.22
Monoclinic, $P2_1$
a = 7.6345 (16) Å
b = 7.7084 (16) Å
c = 12.071 (3) Å
β = 93.17 (1)°
V = 709.3 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.40 mm^{-1}
T = 294 (2) K
0.25 × 0.16 × 0.16 mm

Data collection

Bruker APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.586, T_{max} = 0.701
4398 measured reflections
2424 independent reflections
1787 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.092
S = 1.02
2424 reflections
156 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}
Absolute structure: Flack (1983), with 664 Friedel pairs
Flack parameter: 0.02 (5)

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); 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, 2000); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2560).

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supplementary materials

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(*S*)-2-(Iodomethyl)-1-tosylpyrrolidine

Y.-W. Wang and Y. Peng

Comment

During the past few years, the field of asymmetric catalysis, previously dominated by biocatalysis, has been complemented by organocatalysis (List, 2004; Notz *et al.*, 2004; Allemann *et al.*, 2004) using small organic molecules as a third powerful tool. Organocatalysis reagents are usually non-toxic, highly efficient and selective, readily available, metal-free and robust, explaining the growing interest in their use for organic synthesis (Dalko & Moisan, 2004; Seayed & List, 2005). Considering the above features, low cost and availability in both enantiomeric forms, proline is attractive especially to synthetic chemists. Developed by two industrial laboratories in the early 1970 s (Hajos & Parrish, 1974; Eder *et al.*, 1971), a proline-catalyzed aldol reaction was reinvestigated recently and many novel results were obtained. For example, direct intermolecular asymmetric aldol reactions between aldehydes and the ketones (List *et al.*, 2000; Sakthivel *et al.*, 2001) or aldehydes (Northrup & MacMillan, 2002) afforded good to excellent enantioselectivity. The origin of stereoselectivity in this type of aldol reaction was examined in detail (Bahmanyar *et al.*, 2003) and it was generally accepted this involved enamine intermediates. Similar mechanisms are found in type-1 aldolases (Machajewski & Wong, 2000) and catalytic antibodies that are type-1 aldolase mimics (Wagner *et al.*, 1995; Barbas *et al.*, 1997).

The molecular structure of the title compound (Fig.1) contains a pyrrolidine ring, which exists in an envelope conformation. The dihedral angle between the plane of atoms N1–C1–C3–C5 and the benzene ring is 75.5 (4) °, which potentially provides enough space as a binding-site for substrates during asymmetric catalysis process.

Experimental

The title compound was prepared by the cascade reaction of *p*-toluenesulfonyl chloride with (S)-prolinol (commercial available) and iodine. ^{1}H NMR (400 MHz, $CDCl_3$): 7.73 (d, J = 6.8 Hz, 2H), 7.34 (d, J = 6.8 Hz, 2H), 3.77–3.71 (m, 1H), 3.63–3.60 (m, 1H), 3.51–3.46 (m, 1H), 3.23 (t, J = 9.6 Hz, 2H), 2.44 (s, 3H), 1.90–1.77 (m, 3H), 1.56–1.50 (m, 1H) p.p.m.; ^{13}C NMR (100 MHz, $CDCl_3$): 143.7, 134.2, 129.8 (2 C), 127.5 (2 C), 60.7, 50.0, 31.9, 23.8, 21.5, 11.5 p.p.m.. Single crystals suitable for X-ray determination were obtained by slow evaporation of a EtOAc solution over a period of several days.

Refinement

All H atoms were placed geometrically (C—H distances were set to 0.98, 0.97, 0.96 and 0.93 A° for atoms CH, CH_2, CH_3, and CH (phenyl), respectively) and refined with a riding model, with U_{iso}(H) = 1.2 or 1.5 times U_{eq}(C).

Figures

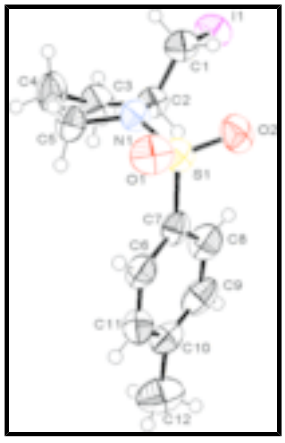

Fig. 1. The molecular structure showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

(*S*)-2-(Iodomethyl)-1-tosylpyrrolidine

Crystal data

$C_{12}H_{16}INO_2S$	F_{000} = 360
M_r = 365.22	D_x = 1.710 Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2yb	Cell parameters from 1240 reflections
a = 7.6345 (16) Å	θ = 3.1–21.5º
b = 7.7084 (16) Å	μ = 2.40 mm^{-1}
c = 12.071 (3) Å	T = 294 (2) K
β = 93.17 (1)º	Block, colorless
V = 709.3 (3) Å^3	0.25 × 0.16 × 0.16 mm
Z = 2	

Data collection

Bruker APEX CCD area-detector diffractometer	2424 independent reflections
Radiation source: fine-focus sealed tube	1787 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.033
T = 294(2) K	θ_{max} = 27.9º
φ and ω scans	θ_{min} = 1.7º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	h = −9→9
T_{min} = 0.586, T_{max} = 0.701	k = −6→9
4398 measured reflections	l = −15→15

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.037$	$w = 1/[\sigma^2(F_o^2) + (0.0387P)^2 + 0.1584P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.092$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.02$	$\Delta\rho_{max} = 0.43$ e Å^{-3}
2424 reflections	$\Delta\rho_{min} = -0.48$ e Å^{-3}
156 parameters	Extinction correction: SHELXL, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
1 restraint	Extinction coefficient: 0.0027 (10)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 664 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.02 (5)

Special details

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}
I1	0.74117 (5)	1.0996 (2)	0.25200 (3)	0.0737 (2)
S1	0.26704 (16)	0.6075 (3)	0.31530 (11)	0.0533 (3)
O2	0.4219 (6)	0.5601 (6)	0.2627 (4)	0.0703 (15)
C2	0.3980 (7)	0.9338 (7)	0.3147 (5)	0.0492 (14)
H2	0.3790	0.9188	0.2343	0.059*
C1	0.5919 (8)	0.9208 (9)	0.3477 (5)	0.0572 (16)
H1A	0.6320	0.8033	0.3355	0.069*
H1B	0.6108	0.9470	0.4260	0.069*
C3	0.3090 (8)	1.0976 (12)	0.3511 (5)	0.0749 (17)
H3A	0.2155	1.1311	0.2977	0.090*
H3B	0.3925	1.1922	0.3594	0.090*
C5	0.1722 (9)	0.8691 (9)	0.4444 (5)	0.0579 (16)
H5A	0.1685	0.8074	0.5143	0.069*
H5B	0.0566	0.8668	0.4068	0.069*
C4	0.2361 (10)	1.0518 (9)	0.4619 (6)	0.074 (2)
H4A	0.3265	1.0578	0.5214	0.089*
H4B	0.1406	1.1287	0.4788	0.089*
N1	0.3058 (6)	0.7944 (6)	0.3740 (4)	0.0484 (11)
O1	0.1979 (6)	0.4989 (6)	0.3981 (4)	0.0676 (12)

C6	−0.0698 (7)	0.5882 (12)	0.2289 (4)	0.0566 (15)
H6	−0.0957	0.5381	0.2962	0.068*
C7	0.1002 (8)	0.6359 (9)	0.2101 (4)	0.0491 (18)
C9	−0.0007 (11)	0.7369 (10)	0.0301 (5)	0.073 (2)
H9	0.0235	0.7888	−0.0369	0.088*
C11	−0.2011 (7)	0.6151 (13)	0.1476 (5)	0.0652 (16)
H11	−0.3147	0.5799	0.1605	0.078*
C10	−0.1693 (9)	0.6917 (9)	0.0491 (5)	0.0614 (17)
C8	0.1366 (10)	0.7067 (9)	0.1096 (5)	0.0651 (19)
H8	0.2514	0.7343	0.0944	0.078*
C12	−0.3186 (12)	0.7276 (15)	−0.0368 (7)	0.107 (3)
H12A	−0.3545	0.8465	−0.0315	0.160*
H12B	−0.4160	0.6532	−0.0233	0.160*
H12C	−0.2795	0.7057	−0.1097	0.160*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0663 (3)	0.0651 (3)	0.0898 (3)	−0.0125 (3)	0.00491 (18)	0.0064 (3)
S1	0.0550 (7)	0.0350 (7)	0.0701 (8)	0.0009 (11)	0.0039 (6)	−0.0016 (12)
O2	0.062 (2)	0.042 (4)	0.107 (3)	0.006 (2)	0.007 (2)	−0.016 (2)
C2	0.060 (4)	0.032 (3)	0.056 (3)	0.001 (3)	0.000 (3)	0.003 (3)
C1	0.062 (4)	0.047 (4)	0.062 (4)	−0.006 (3)	−0.002 (3)	0.002 (3)
C3	0.079 (4)	0.036 (3)	0.111 (5)	−0.002 (5)	0.020 (3)	0.004 (6)
C5	0.067 (4)	0.050 (4)	0.058 (4)	0.002 (3)	0.009 (3)	−0.005 (3)
C4	0.082 (5)	0.050 (5)	0.094 (5)	0.000 (3)	0.022 (4)	−0.025 (4)
N1	0.052 (3)	0.035 (3)	0.058 (3)	0.000 (2)	0.003 (2)	−0.002 (2)
O1	0.084 (3)	0.042 (3)	0.076 (3)	−0.006 (2)	−0.004 (2)	0.016 (2)
C6	0.064 (3)	0.055 (4)	0.052 (3)	−0.013 (4)	0.014 (2)	−0.010 (4)
C7	0.062 (3)	0.036 (5)	0.050 (3)	−0.006 (3)	0.013 (2)	−0.004 (3)
C9	0.109 (6)	0.070 (5)	0.042 (4)	−0.012 (4)	0.007 (4)	−0.002 (3)
C11	0.059 (3)	0.067 (5)	0.070 (4)	0.004 (5)	0.011 (3)	−0.012 (5)
C10	0.075 (4)	0.056 (4)	0.053 (4)	−0.002 (3)	−0.002 (3)	−0.012 (3)
C8	0.074 (4)	0.063 (5)	0.061 (4)	−0.024 (4)	0.021 (3)	−0.005 (3)
C12	0.110 (7)	0.118 (8)	0.089 (6)	−0.007 (6)	−0.028 (5)	−0.001 (5)

Geometric parameters (Å, °)

I1—C1	2.163 (6)	C5—H5B	0.9700
S1—O2	1.420 (4)	C4—H4A	0.9700
S1—O1	1.427 (4)	C4—H4B	0.9700
S1—N1	1.625 (5)	C6—C11	1.379 (8)
S1—C7	1.762 (6)	C6—C7	1.380 (8)
C2—N1	1.490 (7)	C6—H6	0.9300
C2—C3	1.511 (10)	C7—C8	1.372 (8)
C2—C1	1.515 (8)	C9—C10	1.366 (10)
C2—H2	0.9800	C9—C8	1.401 (10)
C1—H1A	0.9700	C9—H9	0.9300
C1—H1B	0.9700	C11—C10	1.361 (9)

C3—C4	1.518 (9)	C11—H11	0.9300
C3—H3A	0.9700	C10—C12	1.523 (10)
C3—H3B	0.9700	C8—H8	0.9300
C5—N1	1.480 (7)	C12—H12A	0.9600
C5—C4	1.502 (9)	C12—H12B	0.9600
C5—H5A	0.9700	C12—H12C	0.9600
O2—S1—O1	120.8 (3)	C3—C4—H4A	111.1
O2—S1—N1	106.7 (3)	C5—C4—H4B	111.1
O1—S1—N1	106.3 (3)	C3—C4—H4B	111.1
O2—S1—C7	107.2 (3)	H4A—C4—H4B	109.1
O1—S1—C7	107.3 (3)	C5—N1—C2	110.8 (4)
N1—S1—C7	108.1 (3)	C5—N1—S1	118.7 (4)
N1—C2—C3	103.3 (5)	C2—N1—S1	120.6 (4)
N1—C2—C1	107.9 (5)	C11—C6—C7	119.7 (6)
C3—C2—C1	115.3 (5)	C11—C6—H6	120.1
N1—C2—H2	110.0	C7—C6—H6	120.1
C3—C2—H2	110.0	C8—C7—C6	119.3 (6)
C1—C2—H2	110.0	C8—C7—S1	120.8 (5)
C2—C1—I1	110.7 (4)	C6—C7—S1	119.8 (4)
C2—C1—H1A	109.5	C10—C9—C8	121.2 (6)
I1—C1—H1A	109.5	C10—C9—H9	119.4
C2—C1—H1B	109.5	C8—C9—H9	119.4
I1—C1—H1B	109.5	C10—C11—C6	122.0 (6)
H1A—C1—H1B	108.1	C10—C11—H11	119.0
C2—C3—C4	104.8 (6)	C6—C11—H11	119.0
C2—C3—H3A	110.8	C11—C10—C9	118.2 (6)
C4—C3—H3A	110.8	C11—C10—C12	120.7 (7)
C2—C3—H3B	110.8	C9—C10—C12	121.1 (7)
C4—C3—H3B	110.8	C7—C8—C9	119.4 (6)
H3A—C3—H3B	108.9	C7—C8—H8	120.3
N1—C5—C4	102.5 (5)	C9—C8—H8	120.3
N1—C5—H5A	111.3	C10—C12—H12A	109.5
C4—C5—H5A	111.3	C10—C12—H12B	109.5
N1—C5—H5B	111.3	H12A—C12—H12B	109.5
C4—C5—H5B	111.3	C10—C12—H12C	109.5
H5A—C5—H5B	109.2	H12A—C12—H12C	109.5
C5—C4—C3	103.1 (6)	H12B—C12—H12C	109.5
C5—C4—H4A	111.1		
N1—C2—C1—I1	173.7 (4)	C7—S1—N1—C2	−72.0 (5)
C3—C2—C1—I1	−71.5 (6)	C11—C6—C7—C8	−1.2 (12)
N1—C2—C3—C4	24.5 (7)	C11—C6—C7—S1	178.1 (7)
C1—C2—C3—C4	−92.9 (7)	O2—S1—C7—C8	−36.5 (7)
N1—C5—C4—C3	36.7 (7)	O1—S1—C7—C8	−167.6 (6)
C2—C3—C4—C5	−38.7 (7)	N1—S1—C7—C8	78.2 (6)
C4—C5—N1—C2	−22.3 (7)	O2—S1—C7—C6	144.1 (6)
C4—C5—N1—S1	−168.3 (5)	O1—S1—C7—C6	13.0 (7)
C3—C2—N1—C5	−1.4 (6)	N1—S1—C7—C6	−101.2 (7)
C1—C2—N1—C5	121.1 (5)	C7—C6—C11—C10	−1.5 (14)

C3—C2—N1—S1	143.9 (4)	C6—C11—C10—C9	2.3 (13)
C1—C2—N1—S1	−93.6 (5)	C6—C11—C10—C12	−177.0 (8)
O2—S1—N1—C5	−174.4 (4)	C8—C9—C10—C11	−0.3 (11)
O1—S1—N1—C5	−44.3 (5)	C8—C9—C10—C12	179.0 (7)
C7—S1—N1—C5	70.6 (5)	C6—C7—C8—C9	3.1 (11)
O2—S1—N1—C2	43.0 (5)	S1—C7—C8—C9	−176.3 (5)
O1—S1—N1—C2	173.1 (4)	C10—C9—C8—C7	−2.4 (11)

Fig. 1