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tert-Butyl 3-(4-bromophenylsulfonyl)-pyrrolidine-1-carboxylate

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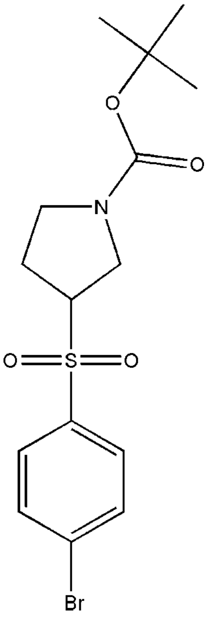
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.032; wR factor = 0.073; data-to-parameter ratio = 16.8.

In the title compound, $C_{15}H_{20}BrNO_4S$, the crystal packing is stabilized by C—H···O hydrogen bonds and van der Waals interactions. The pyrrolidine ring adopts an envelope conformation.

Related literature

The preparation of a similar compound, 4-(4-bromobenzene)sulfonylpiperidine-1-carboxylic acid *tert*-butyl ester, was reported by Fletcher *et al.* (2002).



Experimental

Crystal data

$C_{15}H_{20}BrNO_4S$
M_r = 390.29
Tetragonal, $P\bar{4}2_1c$
a = 18.424 (1) Å
c = 10.108 (1) Å
V = 3431.2 (5) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 2.53 mm^{-1}
T = 293 (2) K
0.33 × 0.26 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
T_{min} = 0.493, T_{max} = 0.707
18794 measured reflections
3390 independent reflections
2760 reflections with $I > 2\sigma(I)$
R_{int} = 0.056

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.073
S = 1.00
3390 reflections
202 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Absolute structure: Flack (1983), 1482 Friedel pairs
Flack parameter: −0.021 (8)

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

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···O1	0.93	2.54	2.916 (3)	105
C7—H7···O3^{i}	0.98	2.27	3.129 (3)	145
C13—H13A···O3	0.96	2.50	3.016 (4)	114
C15—H15C···O3	0.96	2.47	2.996 (6)	115

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2003); 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, 1997); 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: KP2116).

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supplementary materials

Acta Cryst. (2007). E**63**, o3485 [**doi:10.1107/S1600536807032369**]

tert-Butyl 3-(4-bromophenylsulfonyl)pyrrolidine-1-carboxylate

Z. Yao, Z.-G. Li, J.-C. Deng and **J.-W. Xu**

Comment

The title compound, (I), is an intermediate in potential drug synthesis. The pyrrolidine ring adopts an envelope conformation (Fig. 1) with the atom C8 as the flap atom whereas the four atoms are coplanar. The crystal structure is stabilized by C—H···O hydrogen bonds (Fig. 2 and Table 1) and Br···O van der Waals interactions with the distance of 3.126 Å which is shorter than the sum of radii (3.37 Å).

Experimental

Methanesulfonyl chloride (1.26 g, 11 mmol) was added into a mixture of 3-hydroxypyrrolidine-1-carboxylic acid *tert*-butyl ester (1.87 g, 10 mmol) and triethylamine (1.21 g, 12 mmol) in dichloromethane (20 ml) with stirring in an ice bath. The mixture was stirred at 273 K for 1 h, and then warmed to room temperature, stirred for additional 8 h, then partitioned between ethyl acetate (3×15 ml) and water (15 ml). The organic phase was dried and concentrated to give 3-(methylsulfonyloxy)pyrrolidine-1-carboxylic acid *tert*-butyl ester 2.44 g (yield 92%) that was added into a mixture of 4-bromothiophenol (2.27 g, 12 mmol) and potassium carbonate (2.21 g, 16 mmol) in acetonitrile (20 ml), and the resulting slurry was heated at reflux for 24 h. After cooling to room temperature, the reaction mixture was partitioned between water and dichloromethane. The organic phase was washed with brine, dried, and concentrated to give 3-(4-bromobenzene)thiopyrrolidine-1-carboxylic acid *tert*-butyl ester 2.40 g (yield 67%) and then dissolved in 10 ml of methanol; potassium peroxymonosulfate (18.54 g, 30 mmol) was added to a methanol solution. After stirring over 24 h, the solvent was evaporated. The residue was partitioned between chloroform and water. The organic phase was dried and concentrated to give the aimed product as a white solid 2.49 g (yield 92%). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a dichloromethane solution at room temperature.

Refinement

H atoms were found in difference Fourier maps and refined as riding, with C—H distance of 0.93 (aromatic), 0.98 (CH), 0.97 (CH_2) and 0.96 Å (CH_3), and with $U_{iso}(H) = kU_{eq}(C,N)$, where k=1.5 for the methyl groups and k=1.2 for all other H atoms.

Figures

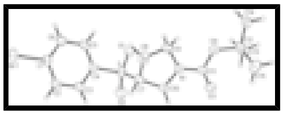

Fig. 1. A view of (I) with the atom-labeling scheme and the 30% probability displacement ellipsoids.

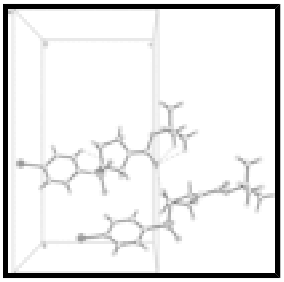

Fig. 2. Crystal packing of (I) viewed along the c axes with hydrogen bonding. For the sake of clarity, H atoms not involved in the hydrogen bonding have been omitted.

tert-Butyl 3-(4-bromophenylsulfonyl)pyrrolidine-1-carboxylate

Crystal data

$C_{15}H_{20}BrNO_4S$

$M_r = 390.29$

Tetragonal, $P\bar{4}2_1c$

$a = 18.4240\ (10)$ Å

$b = 18.4240\ (10)$ Å

$c = 10.1082\ (11)$ Å

$\alpha = 90°$

$\beta = 90°$

$\gamma = 90°$

$V = 3431.2\ (5)$ Å^3

$Z = 8$

$F_{000} = 1600$

$D_x = 1.511$ Mg m$^{-3$}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Cell parameters from 5667 reflections

$\theta = 2.3–23.3°$

$\mu = 2.53$ mm^{-1}

$T = 293\ (2)$ K

Block, colourless

0.33 × 0.26 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293(2)$ K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2002)

$T_{min} = 0.493$, $T_{max} = 0.707$

18794 measured reflections

3390 independent reflections

2760 reflections with $I > 2\sigma(I)$

$R_{int} = 0.056$

$\theta_{max} = 26.1°$

$\theta_{min} = 1.6°$

$h = -22\rightarrow12$

$k = -20\rightarrow22$

$l = -12\rightarrow12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.073$

$S = 1.00$

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.42$ e Å^{-3}

3390 reflections	$\Delta\rho_{\min} = -0.17$ e Å^{-3}
202 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 1482 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: −0.021 (8)

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 $F^2 > 2\text{sigma}(F^2)$ 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}
Br1	0.620575 (19)	0.59671 (2)	−0.04350 (4)	0.06539 (13)
S	0.66889 (4)	0.63796 (4)	0.57777 (8)	0.0515 (2)
C1	0.63226 (15)	0.60962 (17)	0.1410 (3)	0.0468 (7)
O1	0.61910 (12)	0.59169 (13)	0.6474 (2)	0.0652 (6)
O3	0.83317 (15)	0.59393 (12)	0.9922 (2)	0.0746 (7)
C3	0.68573 (17)	0.67391 (17)	0.3186 (3)	0.0510 (8)
H3	0.7146	0.7115	0.3502	0.061*
O2	0.66995 (16)	0.71375 (13)	0.6072 (2)	0.0772 (7)
O4	0.80675 (12)	0.47438 (10)	0.9672 (2)	0.0591 (6)
C9	0.75873 (19)	0.49303 (17)	0.7196 (3)	0.0564 (8)
H9A	0.7084	0.4848	0.7434	0.068*
H9B	0.7854	0.4479	0.7282	0.068*
C4	0.65312 (15)	0.62685 (16)	0.4064 (3)	0.0459 (7)
N1	0.79046 (14)	0.54924 (13)	0.7999 (3)	0.0508 (6)
C6	0.59860 (17)	0.56282 (18)	0.2270 (3)	0.0538 (8)
H6	0.5690	0.5258	0.1952	0.065*
C5	0.60938 (17)	0.57141 (16)	0.3618 (3)	0.0513 (8)
H5	0.5873	0.5400	0.4216	0.062*
C8	0.7650 (2)	0.52323 (18)	0.5805 (3)	0.0630 (9)
H8A	0.8112	0.5102	0.5411	0.076*
H8B	0.7261	0.5051	0.5248	0.076*
C12	0.83221 (17)	0.45220 (17)	1.0991 (3)	0.0534 (8)
C11	0.81189 (17)	0.54343 (16)	0.9263 (3)	0.0527 (8)
C7	0.75911 (16)	0.60457 (18)	0.5981 (3)	0.0534 (8)
H7	0.7910	0.6286	0.5339	0.064*
C10	0.78683 (18)	0.62034 (18)	0.7381 (3)	0.0562 (8)
H10A	0.8343	0.6430	0.7356	0.067*
H10B	0.7536	0.6519	0.7854	0.067*

C2	0.67588 (17)	0.66560 (17)	0.1851 (3)	0.0512 (8)
H2	0.6981	0.6970	0.1255	0.061*
C14	0.8185 (2)	0.37114 (18)	1.0985 (4)	0.0701 (10)
H14A	0.7677	0.3621	1.0850	0.105*
H14B	0.8333	0.3508	1.1817	0.105*
H14C	0.8459	0.3491	1.0284	0.105*
C13	0.7871 (2)	0.4881 (2)	1.2038 (4)	0.0810 (11)
H13A	0.8001	0.5385	1.2097	0.121*
H13B	0.7957	0.4650	1.2874	0.121*
H13C	0.7367	0.4839	1.1812	0.121*
C15	0.9123 (2)	0.4685 (3)	1.1138 (5)	0.0936 (14)
H15A	0.9379	0.4509	1.0374	0.140*
H15B	0.9306	0.4448	1.1916	0.140*
H15C	0.9192	0.5199	1.1216	0.140*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0659 (2)	0.0847 (3)	0.04548 (16)	0.00603 (17)	−0.00009 (17)	0.00048 (18)
S	0.0526 (5)	0.0572 (5)	0.0447 (4)	0.0067 (4)	0.0066 (4)	−0.0020 (3)
C1	0.0444 (17)	0.0557 (19)	0.0402 (14)	0.0114 (16)	0.0003 (13)	0.0023 (14)
O1	0.0509 (12)	0.0935 (17)	0.0512 (12)	0.0015 (15)	0.0106 (11)	0.0073 (12)
O3	0.1084 (18)	0.0532 (13)	0.0621 (15)	−0.0231 (14)	−0.0227 (13)	0.0004 (11)
C3	0.0526 (18)	0.0429 (17)	0.0577 (19)	0.0007 (15)	0.0012 (15)	0.0030 (16)
O2	0.105 (2)	0.0596 (15)	0.0674 (16)	0.0173 (15)	−0.0021 (15)	−0.0141 (12)
O4	0.0740 (15)	0.0450 (12)	0.0584 (14)	−0.0080 (10)	−0.0145 (12)	0.0049 (11)
C9	0.068 (2)	0.0424 (16)	0.0587 (19)	0.0013 (16)	−0.0070 (17)	−0.0107 (16)
C4	0.0426 (17)	0.0482 (18)	0.0468 (16)	0.0082 (15)	0.0050 (13)	0.0002 (14)
N1	0.0574 (15)	0.0424 (13)	0.0526 (15)	−0.0097 (12)	−0.0044 (13)	0.0019 (12)
C6	0.0514 (19)	0.0591 (19)	0.0510 (18)	−0.0020 (16)	0.0006 (15)	−0.0031 (15)
C5	0.0499 (19)	0.0507 (18)	0.0534 (18)	−0.0031 (15)	0.0074 (15)	0.0090 (14)
C8	0.061 (2)	0.071 (2)	0.056 (2)	0.0140 (17)	−0.0035 (16)	−0.0140 (17)
C12	0.0533 (19)	0.0502 (18)	0.0566 (19)	0.0048 (16)	−0.0085 (15)	0.0051 (15)
C11	0.0588 (19)	0.0431 (17)	0.056 (2)	−0.0081 (15)	−0.0050 (16)	−0.0003 (15)
C7	0.0474 (17)	0.065 (2)	0.0472 (16)	−0.0050 (16)	0.0070 (14)	0.0041 (15)
C10	0.0614 (19)	0.0516 (18)	0.0556 (19)	−0.0159 (17)	−0.0039 (15)	0.0101 (16)
C2	0.0493 (17)	0.0537 (18)	0.0506 (18)	0.0014 (16)	0.0062 (15)	0.0129 (15)
C14	0.080 (2)	0.050 (2)	0.080 (3)	0.0036 (19)	−0.017 (2)	0.0083 (17)
C13	0.099 (3)	0.074 (2)	0.070 (2)	0.016 (2)	0.015 (2)	0.010 (2)
C15	0.054 (2)	0.102 (3)	0.125 (4)	−0.004 (2)	−0.022 (2)	0.013 (3)

Geometric parameters (Å, °)

Br1—C1	1.893 (3)	C5—H5	0.9300
S—O2	1.428 (2)	C8—C7	1.513 (5)
S—O1	1.437 (2)	C8—H8A	0.9700
S—C4	1.768 (3)	C8—H8B	0.9700
S—C7	1.784 (3)	C12—C13	1.499 (5)
C1—C6	1.372 (4)	C12—C15	1.513 (5)

C1—C2	1.381 (4)	C12—C14	1.515 (5)
O3—C11	1.210 (4)	C7—C10	1.533 (4)
C3—C2	1.370 (5)	C7—H7	0.9800
C3—C4	1.378 (4)	C10—H10A	0.9700
C3—H3	0.9300	C10—H10B	0.9700
O4—C11	1.341 (4)	C2—H2	0.9300
O4—C12	1.472 (4)	C14—H14A	0.9600
C9—N1	1.440 (4)	C14—H14B	0.9600
C9—C8	1.516 (4)	C14—H14C	0.9600
C9—H9A	0.9700	C13—H13A	0.9600
C9—H9B	0.9700	C13—H13B	0.9600
C4—C5	1.377 (4)	C13—H13C	0.9600
N1—C11	1.342 (4)	C15—H15A	0.9600
N1—C10	1.452 (4)	C15—H15B	0.9600
C6—C5	1.386 (4)	C15—H15C	0.9600
C6—H6	0.9300		

O2—S—O1	119.13 (16)	O4—C12—C14	102.5 (3)
O2—S—C4	108.65 (15)	C13—C12—C14	110.2 (3)
O1—S—C4	107.84 (14)	C15—C12—C14	111.0 (3)
O2—S—C7	107.49 (17)	O3—C11—O4	125.7 (3)
O1—S—C7	109.51 (14)	O3—C11—N1	123.9 (3)
C4—S—C7	103.05 (13)	O4—C11—N1	110.4 (3)
C6—C1—C2	121.9 (3)	C8—C7—C10	105.8 (3)
C6—C1—Br1	119.6 (2)	C8—C7—S	113.2 (2)
C2—C1—Br1	118.6 (2)	C10—C7—S	110.6 (2)
C2—C3—C4	120.4 (3)	C8—C7—H7	109.0
C2—C3—H3	119.8	C10—C7—H7	109.0
C4—C3—H3	119.8	S—C7—H7	109.0
C11—O4—C12	121.4 (2)	N1—C10—C7	104.0 (3)
N1—C9—C8	103.2 (3)	N1—C10—H10A	111.0
N1—C9—H9A	111.1	C7—C10—H10A	111.0
C8—C9—H9A	111.1	N1—C10—H10B	111.0
N1—C9—H9B	111.1	C7—C10—H10B	111.0
C8—C9—H9B	111.1	H10A—C10—H10B	109.0
H9A—C9—H9B	109.1	C3—C2—C1	118.6 (3)
C5—C4—C3	120.7 (3)	C3—C2—H2	120.7
C5—C4—S	120.2 (2)	C1—C2—H2	120.7
C3—C4—S	119.1 (2)	C12—C14—H14A	109.5
C11—N1—C9	126.8 (3)	C12—C14—H14B	109.5
C11—N1—C10	119.6 (3)	H14A—C14—H14B	109.5
C9—N1—C10	112.8 (3)	C12—C14—H14C	109.5
C1—C6—C5	119.1 (3)	H14A—C14—H14C	109.5
C1—C6—H6	120.5	H14B—C14—H14C	109.5
C5—C6—H6	120.5	C12—C13—H13A	109.5
C4—C5—C6	119.4 (3)	C12—C13—H13B	109.5
C4—C5—H5	120.3	H13A—C13—H13B	109.5
C6—C5—H5	120.3	C12—C13—H13C	109.5
C7—C8—C9	104.4 (3)	H13A—C13—H13C	109.5
C7—C8—H8A	110.9	H13B—C13—H13C	109.5

C9—C8—H8A	110.9	C12—C15—H15A	109.5
C7—C8—H8B	110.9	C12—C15—H15B	109.5
C9—C8—H8B	110.9	H15A—C15—H15B	109.5
H8A—C8—H8B	108.9	C12—C15—H15C	109.5
O4—C12—C13	109.9 (3)	H15A—C15—H15C	109.5
O4—C12—C15	110.2 (3)	H15B—C15—H15C	109.5
C13—C12—C15	112.6 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O1	0.93	2.54	2.916 (3)	105
C7—H7···O3^{i}	0.98	2.27	3.129 (3)	145
C13—H13A···O3	0.96	2.50	3.016 (4)	114
C15—H15C···O3	0.96	2.47	2.996 (6)	115

Symmetry codes: (i) $-y+3/2, -x+3/2, z-1/2$.

Fig. 1

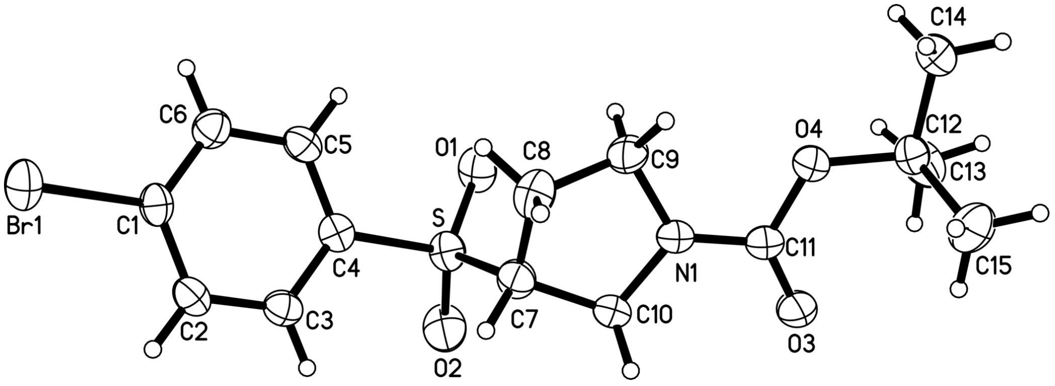
C14
C12
O4
C13
O1
C8
C9
C6
C5
C15
Br1
C1
C4
S
C11
N1
C7
C10
C2
C3
O3
O2

Fig. 2