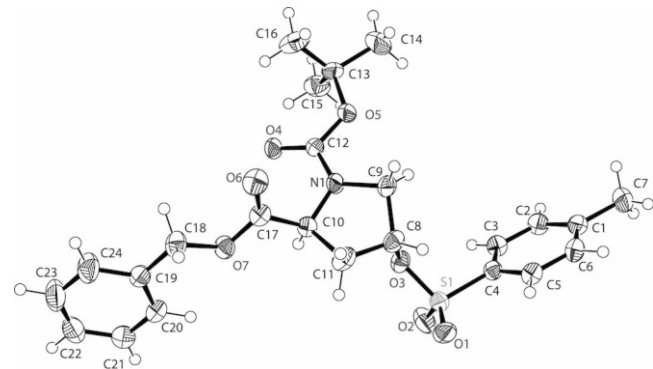


Crystal structure of (2*S*, 4*R*)-2-benzyl 1-*tert*-butyl 4-(tosyloxy)pyrrolidine-1,2-dicarboxylate, C₂₄H₂₉NO₇S

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Abstract

C₂₄H₂₉NO₇S, triclinic, *P*1 (no. 1), *a* = 6.5903(3) Å, *b* = 9.7193(5) Å, *c* = 9.9874(4) Å, α = 82.462(4)°, β = 77.197(3)°, γ = 85.6180(4)°, *V* = 617.7 Å³, *Z* = 1, *R*_{gt}(*F*) = 0.0351, *wR*_{ref}(*F*²) = 0.0967, *T* = 123 K.

Table 1. Data collection and handling.

Crystal:	colourless prisms, size 0.1551×0.2145×0.3113 mm
Wavelength:	Cu K α radiation (1.54184 Å)
μ :	15.30 cm ⁻¹
Diffractometer, scan mode:	SuperNova System, ω
2 θ _{max} :	147.46°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	22769, 4737
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ (<i>I</i> _{obs}), 4714
<i>N</i> (<i>param</i>) _{refined} :	298
Programs:	SIR-97 [4], SHELXL-97 [5], PLATON [6]

Source of material

All chemicals were purchased from commercial suppliers and used without further purification. The title compound was synthesized following the general procedure reported in the literature [1]. *p*-Toluenesulfonyl chloride (1.31 g, 6.84 mmol) was added portionwise to a solution of 2-benzyl 1-*tert*-butyl (2*S*,4*R*)-4-hydroxypyrrolidine-1,2-dicarboxylate [2] (2 g, 6.22 mmol) in pyridine (10 mL) at 0 °C. The mixture was stirred for 12 h at room temperature, the solvent evaporated in vacuo and the residue poured into an ice bath. The mixture was extracted with ethyl acetate (3 × 50 mL) and washed subsequently with 1M HCl, H₂O, Na₂CO₃ (10%) and H₂O. The combined organic phases were dried over anhydrous Na₂SO₄, filtered and the solvent evaporated to give a yellow oil, which was purified by column chromatography (eluent = hexane:ethyl acetate 8:2). The title compound was obtained as a colourless oil (yield 75%) and displayed spectroscopic data identical to those reported in the literature [3]. The compound spontaneously crystallized over time to white crystals

suitable for X-ray analysis (m.p. 76–77 °C). An Ortep diagram with ellipsoids drawn at the 50% probability level is shown.

Experimental details

The data were collected at 123K using an Oxford Instruments Cryojet Cooler. The structure was solved by direct methods (SIR-97 [4]) and refined by full-matrix anisotropic least squares (SHELXL-97 [5]).

All hydrogen atoms on carbons were generated geometrically with *d*(C–H) = 0.95–1.00 Å and *U*_{iso}(H) = 1.28 *U*_{eq}(C).

Discussion

Substituted prolines have attracted a great deal of attention in the development of molecular probes, ligands, and asymmetric organocatalysts [3]. In the title compound, the characteristic C=O, C–O and C–N bond distances are in the ranges 1.217(2)–1.197(2) Å, 1.332(2)–1.482(2) Å and 1.354(2)–1.464(3) Å, respectively. The C–S bond distance is 1.7560(19) Å. The characteristic $\angle$ O–C–C, $\angle$ O–S–C and $\angle$ C–N–C bond angles are in the ranges 102.22–125.48°, 105.17–108.76° and 113.48–125.84°, respectively. Other bond distances and angles are all in normal ranges. The molecular structure is further extended through intermolecular CH–O interactions (H–O bond distances are in the range 2.352(1)–2.715(1) Å) and CH– π interactions (centroid–H distances are 3.150 and 3.082 Å).

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(2)	1 <i>a</i>	0.4169	−0.0555	0.7089	0.045
H(3)	1 <i>a</i>	0.2365	0.1057	0.5796	0.04
H(5)	1 <i>a</i>	0.7837	0.2138	0.3212	0.039
H(6)	1 <i>a</i>	0.9613	0.0508	0.4516	0.044
H(7A)	1 <i>a</i>	0.7744	−0.2185	0.6763	0.063
H(7B)	1 <i>a</i>	0.7987	−0.1032	0.7716	0.063
H(7C)	1 <i>a</i>	0.9732	−0.1247	0.6354	0.063
H(8)	1 <i>a</i>	0.4911	0.1747	0.1141	0.042
H(9A)	1 <i>a</i>	0.3662	−0.0281	0.0678	0.05
H(9B)	1 <i>a</i>	0.2568	−0.0288	0.2293	0.05
H(10)	1 <i>a</i>	−0.0799	0.2401	0.1016	0.035
H(11A)	1 <i>a</i>	0.3297	0.2442	−0.0716	0.046
H(11B)	1 <i>a</i>	0.223	0.3528	0.0353	0.046
H(14A)	1 <i>a</i>	−0.1169	−0.4765	0.325	0.082
H(14B)	1 <i>a</i>	0.0042	−0.3603	0.3711	0.082
H(14C)	1 <i>a</i>	0.0886	−0.4158	0.2239	0.082
H(15A)	1 <i>a</i>	−0.3234	−0.2104	0.4102	0.061
H(15B)	1 <i>a</i>	−0.4447	−0.3262	0.3637	0.061
H(15C)	1 <i>a</i>	−0.4462	−0.1706	0.288	0.061

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Table 2. continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(16A)	1a	−0.2955	−0.4074	0.1216	0.07
H(16B)	1a	−0.0886	−0.3384	0.031	0.07
H(16C)	1a	−0.3036	−0.2477	0.058	0.07
H(18A)	1a	−0.2665	0.2438	−0.2762	0.049
H(18B)	1a	−0.099	0.3617	−0.3263	0.049

Table 2. continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(20)	1a	−0.3461	0.5183	−0.0725	0.052
H(21)	1a	−0.6241	0.6823	−0.0573	0.06
H(22)	1a	−0.8358	0.7059	−0.2182	0.061
H(23)	1a	−0.7739	0.5589	−0.3914	0.074
H(24)	1a	−0.496	0.3942	−0.4069	0.065

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
S(1)	1a	0.35568(5)	0.29985(4)	0.34512(4)	0.0409(2)	0.0305(2)	0.0327(2)	−0.0020(2)	−0.0141(2)	0.0011(2)
O(1)	1a	0.5015(3)	0.3823(2)	0.2459(2)	0.063(1)	0.0363(8)	0.0454(8)	−0.0202(7)	−0.0259(7)	0.0126(6)
O(2)	1a	0.1956(3)	0.3629(2)	0.4421(2)	0.0607(9)	0.0487(9)	0.0453(8)	0.0200(7)	−0.0200(7)	−0.0115(7)
O(3)	1a	0.2320(2)	0.2161(1)	0.2668(1)	0.0280(6)	0.0407(8)	0.0329(6)	−0.0059(5)	−0.0075(5)	−0.0012(5)
O(4)	1a	−0.2583(2)	−0.0116(1)	0.0989(1)	0.0251(6)	0.0338(7)	0.0443(7)	−0.0041(5)	−0.0131(5)	0.0026(5)
O(5)	1a	−0.0284(2)	−0.1629(1)	0.1902(2)	0.0380(7)	0.0254(7)	0.0650(9)	−0.0039(5)	−0.0260(6)	0.0023(6)
O(6)	1a	0.0331(2)	0.1131(2)	−0.1843(2)	0.0408(7)	0.0527(9)	0.0342(7)	0.0021(6)	−0.0017(5)	−0.0145(6)
O(7)	1a	−0.1579(2)	0.3039(2)	−0.1205(1)	0.0434(7)	0.0400(8)	0.0263(6)	0.0019(6)	−0.0117(5)	−0.0056(6)
N(1)	1a	0.0643(2)	0.0492(2)	0.0999(2)	0.0203(7)	0.0309(8)	0.0454(8)	−0.0028(5)	−0.0108(6)	0.0008(6)
C(1)	1a	0.7078(3)	−0.0201(2)	0.5930(2)	0.039(1)	0.033(1)	0.0367(9)	−0.0018(7)	−0.0137(8)	−0.0040(7)
C(2)	1a	0.4915(3)	−0.0014(2)	0.6296(2)	0.0390(9)	0.039(1)	0.0311(9)	−0.0074(7)	−0.0061(7)	0.0061(7)
C(3)	1a	0.3838(3)	0.0939(2)	0.5532(2)	0.0299(8)	0.038(1)	0.0311(9)	−0.0034(7)	−0.0017(7)	−0.0011(7)
C(4)	1a	0.4934(3)	0.1729(2)	0.4367(2)	0.0315(8)	0.031(1)	0.0259(8)	−0.0025(7)	−0.0078(6)	−0.0025(7)
C(5)	1a	0.7091(3)	0.1583(2)	0.3993(2)	0.0312(8)	0.041(1)	0.0255(8)	−0.0070(7)	−0.0027(6)	−0.0022(7)
C(6)	1a	0.8139(3)	0.0617(2)	0.4774(2)	0.0280(8)	0.046(1)	0.0364(9)	−0.0019(7)	−0.0080(7)	−0.0055(8)
C(7)	1a	0.8237(4)	−0.1259(3)	0.6764(3)	0.052(1)	0.047(1)	0.061(1)	0.001(1)	−0.028(1)	0.006(1)
C(8)	1a	0.3362(3)	0.1697(2)	0.1328(2)	0.0236(8)	0.041(1)	0.0399(9)	−0.0057(7)	−0.0039(7)	−0.0083(8)
C(9)	1a	0.2683(3)	0.0236(2)	0.1362(3)	0.0234(8)	0.039(1)	0.069(1)	0.0018(7)	−0.0193(8)	−0.013(1)
C(10)	1a	0.0301(3)	0.1894(2)	0.0375(2)	0.0269(8)	0.0318(9)	0.0262(8)	−0.0048(6)	−0.0024(6)	−0.0001(7)
C(11)	1a	0.2414(3)	0.2533(2)	0.0212(2)	0.0356(9)	0.048(1)	0.0308(9)	−0.0179(8)	−0.0026(7)	−0.0009(8)
C(12)	1a	−0.0894(3)	−0.0418(2)	0.1280(2)	0.0261(8)	0.0268(9)	0.0371(9)	−0.0029(6)	−0.0100(6)	−0.0026(7)
C(13)	1a	−0.1689(3)	−0.2803(2)	0.2275(2)	0.050(1)	0.0243(9)	0.049(1)	−0.0099(8)	−0.0182(9)	−0.0004(8)
C(14)	1a	−0.0365(5)	−0.3933(3)	0.2926(4)	0.078(2)	0.032(1)	0.100(2)	−0.003(1)	−0.038(2)	0.011(1)
C(15)	1a	−0.3628(4)	−0.2437(3)	0.3314(3)	0.065(1)	0.038(1)	0.046(1)	−0.012(1)	−0.008(1)	0.0024(9)
C(16)	1a	−0.2185(5)	−0.3221(3)	0.0982(3)	0.083(2)	0.048(1)	0.047(1)	−0.030(1)	−0.012(1)	−0.008(1)
C(17)	1a	−0.0296(3)	0.1938(2)	−0.1019(2)	0.0278(8)	0.037(1)	0.0264(8)	−0.0059(7)	−0.0005(6)	−0.0036(7)
C(18)	1a	−0.2190(3)	0.3301(2)	−0.2527(2)	0.046(1)	0.053(1)	0.0263(8)	0.0007(9)	−0.0124(8)	−0.0071(8)
C(19)	1a	−0.3921(3)	0.4400(2)	−0.2417(2)	0.039(1)	0.037(1)	0.0261(8)	−0.0117(8)	−0.0076(7)	0.0045(7)
C(20)	1a	−0.4324(4)	0.5263(2)	−0.1380(2)	0.048(1)	0.041(1)	0.048(1)	−0.0044(9)	−0.0228(9)	−0.0091(9)
C(21)	1a	−0.5976(4)	0.6240(2)	−0.1292(3)	0.056(1)	0.040(1)	0.059(1)	0.002(1)	−0.022(1)	−0.010(1)
C(22)	1a	−0.7240(4)	0.6377(3)	−0.2238(3)	0.049(1)	0.049(1)	0.053(1)	0.002(1)	−0.017(1)	0.008(1)
C(23)	1a	−0.6864(5)	0.5512(3)	−0.3266(3)	0.067(2)	0.073(2)	0.053(1)	0.010(1)	−0.035(1)	−0.003(1)
C(24)	1a	−0.5211(4)	0.4531(3)	−0.3356(2)	0.065(1)	0.068(2)	0.037(1)	0.006(1)	−0.025(1)	−0.009(1)

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