Crystal structure of (*S*)-*tert*-butyl 3-carbamothioyl-3,4-dihydroisoquinoline-2(1*H*)-carboxylate, $C_{63}H_{86}N_8O_9S_4$

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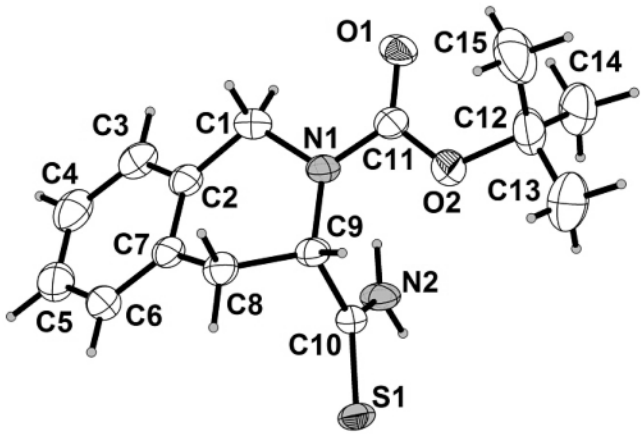

Abstract

$C_{63}H_{86}N_8O_9S_4$, tetragonal, *I*4 (no. 79), a = 22.5939(8) Å, c = 6.6576(4) Å, V = 3398.6(3) Å^3, Z = 2, $R_{gt(F)}$ = 0.0351, $wR_{ref(F^2)}$ = 0.0977, T = 173 K.

Table 1. Data collection and handling.

Crystal:	yellow needles, size 0.11×0.12×0.48 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.97 cm^{-1}
Diffractometer, scan mode:	Bruker SMART ApexII CCD, φ and ω
$2\theta_{max}$:	56.6°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	32732, 4223
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3752
$N(param)_{refined}$:	189
Programs:	SADABS [4], OLEX2 [5], SHELX [7]

Source of material

To a solution of *N*-protected tetrahydroisoquinoline (*TIQ*) amide (0.40 g, 0.89 mmol, 1 eq.) in THF (4 mL) Lawessons reagent (0.20 g, 0.44 mmol, 0.5 eq.) was added, the resultant solution was stirred overnight at room temperature. The reaction was monitored by thin layer chromatography (*TLC*) using MeOH/DCM (5/95, R_f = 0.4). The THF was evaporated under reduced pressure and diluted with ethyl acetate (30 mL) and then washed with water (20 mL). The organic layer was separated and dried over anhydrous $MgSO_4$ and the solvent evaporated under reduced pressure to afford crude carboxybenzyl protected thioamide, which was purified by silica gel column chromatography using 0-1.5 % MeOH in DCM as the eluent to yield 78 % yield of the pure thioamide as a white solid. Melting point = 435-437 K. Crystals suitable for X-ray diffraction were obtained by slow evaporation of the title compound in acetone and hexane at room temperature.

Experimental details

All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were positioned geometrically with d(C–H) ranging from 0.95 Å to 1.00 Å and d(N–H) = 0.88 Å and refined as riding on their parent atoms with U_{iso}(H) = 1.2 - 1.5 U_{eq} (C or N).

Discussion

The title compound is an intermediate on the way to novel *TIQ* ligands. The absolute stereochemistry was confirmed to be *S* at the C9 position from proton NMR and X-ray crystal data [1-3, 6]. From the crystal structure it is evident that the pyridine ring of the *TIQ* backbone is in boat conformation [Q = 0.5640(18) Å, θ = 99.32(18)° and ϕ = 73.70 (18)°]. The torsion angle for C1–N1–C9–C10 is 106.69(16)°. Intermolecular N–H···O=C hydrogen bonding *via* the thioamide group crosslinks the molecules in the crystal structure. The acetone solvate molecule is located on a four-fold axis in the tetragonal space group resulting in a corresponding disorder.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(2A)	8*c*		0.3078	0.2392	0.6454	0.044
H(2B)	8*c*		0.3212	0.2529	0.4258	0.044
H(1A)	8*c*		0.2982	0.1756	1.0429	0.046
H(1B)	8*c*		0.3580	0.1774	1.1711	0.046
H(3)	8*c*		0.2991	0.0707	0.9626	0.047
H(4)	8*c*		0.3419	–0.0084	0.7925	0.054
H(5)	8*c*		0.4328	0.0031	0.6330	0.059
H(6)	8*c*		0.4823	0.0936	0.6473	0.051
H(8A)	8*c*		0.4825	0.1986	0.7386	0.040
H(8B)	8*c*		0.4693	0.1974	0.9748	0.040
H(9)	8*c*		0.4279	0.2837	0.8598	0.035
H(13A)	8*c*		0.3536	0.4309	0.7607	0.135
H(13B)	8*c*		0.4018	0.4294	0.9369	0.135
H(13C)	8*c*		0.3495	0.4771	0.9423	0.135
H(14A)	8*c*		0.2347	0.3689	1.0382	0.115
H(14B)	8*c*		0.2538	0.3884	0.8164	0.115
H(14C)	8*c*		0.2428	0.4375	0.9856	0.115
H(15A)	8*c*		0.3047	0.3721	1.3158	0.114
H(15B)	8*c*		0.3193	0.4409	1.2866	0.114
H(15C)	8*c*		0.3716	0.3931	1.2818	0.114
C(2G)	2*a*		½	½	1.363(3)	0.172(5)
O(1G)	2*a*		½	½	1.184(3)	0.353(9)
C(1G)	8*c*	0.5	0.494(1)	0.4397(6)	1.467(3)	0.268(9)
H(1G1)	8*c*	0.5	0.4945	0.4452	1.6134	0.402
H(1G2)	8*c*	0.5	0.5271	0.4142	1.4278	0.402
H(1G3)	8*c*	0.5	0.4566	0.4211	1.4275	0.402

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	8*c*	0.44062(2)	0.27415(2)	0.42641(8)	0.0401(2)	0.0584(3)	0.0332(2)	0.0043(2)	0.0110(2)	0.0130(2)
O(1)	8*c*	0.28887(5)	0.27987(6)	1.1586(2)	0.0364(6)	0.0559(7)	0.0209(5)	0.0150(5)	–0.0003(5)	–0.0004(5)
O(2)	8*c*	0.34662(6)	0.33613(5)	0.9533(2)	0.0587(7)	0.0382(6)	0.0346(7)	0.0130(5)	0.0062(6)	0.0005(6)
N(1)	8*c*	0.35591(5)	0.23824(6)	0.9475(2)	0.0339(6)	0.0369(6)	0.0201(6)	0.0046(5)	0.0030(5)	0.0015(5)
N(2)	8*c*	0.33334(6)	0.24841(7)	0.5505(2)	0.0330(7)	0.0571(9)	0.0188(6)	0.0067(6)	0.0017(5)	0.0041(6)
C(1)	8*c*	0.34172(8)	0.17976(7)	1.0333(3)	0.0419(9)	0.0408(8)	0.0330(9)	0.0029(7)	0.0116(7)	0.0035(7)
C(2)	8*c*	0.36591(6)	0.12949(7)	0.9114(3)	0.0328(7)	0.0382(7)	0.0240(7)	0.0043(6)	–0.0017(7)	0.0048(7)
C(3)	8*c*	0.33663(8)	0.07544(7)	0.9000(3)	0.0418(8)	0.0437(9)	0.0314(9)	–0.0024(7)	–0.0041(7)	0.0080(7)
C(4)	8*c*	0.3618(1)	0.02863(8)	0.7980(3)	0.065(1)	0.0385(9)	0.0326(9)	–0.0035(8)	–0.0110(9)	0.0032(8)
C(5)	8*c*	0.4157(1)	0.03539(8)	0.7040(3)	0.076(1)	0.0410(9)	0.0311(9)	0.0131(9)	0.0007(9)	–0.0007(8)
C(6)	8*c*	0.44520(9)	0.08913(8)	0.7130(3)	0.048(1)	0.047(1)	0.0325(9)	0.0145(8)	0.0049(8)	0.0066(8)
C(7)	8*c*	0.42079(7)	0.13652(7)	0.8176(3)	0.0322(7)	0.0398(8)	0.0240(8)	0.0076(6)	–0.0008(6)	0.0071(7)
C(8)	8*c*	0.45071(7)	0.19512(7)	0.8403(3)	0.0269(7)	0.0440(9)	0.0297(8)	0.0047(6)	–0.0023(6)	0.0068(7)
C(9)	8*c*	0.40719(7)	0.24687(7)	0.8151(2)	0.0307(7)	0.0362(7)	0.0211(7)	0.0002(6)	0.0010(6)	0.0009(6)
C(10)	8*c*	0.38949(7)	0.25542(7)	0.5949(2)	0.0341(7)	0.0318(7)	0.0224(7)	0.0065(6)	0.0041(6)	0.0024(6)
C(11)	8*c*	0.32768(7)	0.28525(7)	1.0310(2)	0.0367(8)	0.0429(8)	0.0180(7)	0.0088(6)	–0.0051(6)	0.0010(6)
C(12)	8*c*	0.3223(1)	0.39391(9)	1.0201(4)	0.081(2)	0.040(1)	0.053(1)	0.026(1)	0.000(1)	–0.0005(9)
C(13)	8*c*	0.3601(2)	0.4365(1)	0.9050(6)	0.124(2)	0.042(1)	0.104(3)	0.014(1)	0.013(2)	0.013(2)
C(14)	8*c*	0.2577(1)	0.3975(1)	0.9597(5)	0.088(2)	0.077(2)	0.065(2)	0.044(1)	–0.005(1)	0.016(1)
C(15)	8*c*	0.3302(2)	0.4006(1)	1.2463(4)	0.105(2)	0.060(1)	0.062(2)	0.031(1)	–0.011(2)	–0.024(1)

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