Crystal structure of *N*-benzoyl-4,4-dimethyl-2-methylamino-2-thiazoline, $C_{13}H_{16}N_2OS$

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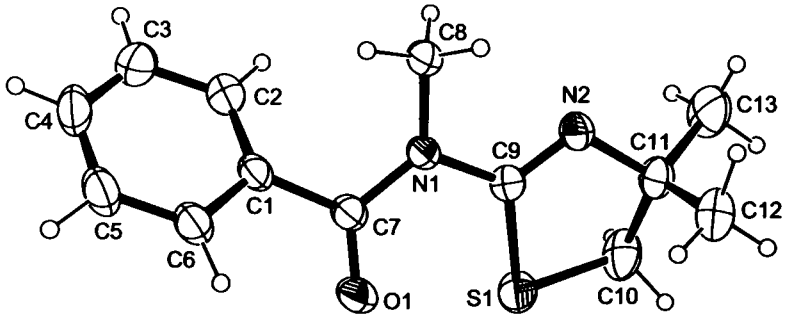

Abstract

$C_{13}H_{16}N_2OS$, monoclinic, *C*12/*c*1 (no. 15),
a = 21.908(2) Å, b = 13.932(2) Å, c = 8.7971(9) Å,
β = 101.952(2)°, V = 2626.9 Å^3, Z = 8, $R_{gt}(F)$ = 0.041,
$wR_{ref}(F^2)$ = 0.113, T = 293 K.

Source of material

The title compound was prepared by the reaction of 2-methylamino-4,4-dimethyl-2-thiazoline with benzoyl chloride in the presence of potassium *tert*-butoxide at room temperature [1]. To a solution of 2-methylamino-4,4-dimethyl-2-thiazoline (0.50 g, 3.45 mmol) and *tert*-BuOK (0.46 g, 4.14 mmol) in dry THF (20 mL) under nitrogen was added benzoyl chloride (0.56 mL, 4.83 mmol) dropwise. After 30 min the reaction mixture was quenched with water (30 mL) and extracted with ether (3 × 50 mL). The organic layer was dried, filtered, evaporated. The crude product was purified by flash column chromatography to give the product.

Discussion

Acylation of the 2-methylamino-2-thiazolines can conceivably proceed through an attack upon acyl halide either by the *exo*-nitrogen to provide *N*-acylated 2-methylamino-2-thiazolines or by the endo-nitrogen to give *N*-acylated 2-methyliminothiazolidines. The reaction of 2-amino-2-thiazolines with some electrophilic compounds was investigated in detail by Avalos et al. [2]. The question of regioselective functionalization of both nitrogen atoms has been the subject of reasonable controversy in the literature over the years [3]. At present, it has been accepted that the endo regiospecificity appears to be general. However, the reaction of 2-methylamino-4,4-dimethyl-2-thiazoline with benzoyl chloride furnished regioselectively the exo-substituted title compound.

In the crystal structure, the five-membered thiazoline ring reveals an envelope conformation. The four atoms (S1, C9, N2 and C11) lie on a plane with the torsion angle ∠C11–N2–C9–S1 = –3.99(17)°, and the C10 atom is 0.46 Å apart from the plane. Examination of the structure with PLATON [4] reveals a short ring-interaction (< 6 Å) for phenyl rings. The centroid-centroid distance between Cg1 (the centroid of the phenyl ring C1-C6) and Cg1^{i} (symmetry code i: x,–y,–½+z) is 5.272 Å, and the dihedral angle between the ring planes is 76.6°.

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Table 1. Data collection and handling.

Crystal:	colorless needle, size 0.09 × 0.10 × 0.10 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.32 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	56.52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8102, 3067
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2097
$N(param)_{refined}$:	218
Programs:	PLATON [4], SHELXS-97 [5], SHELXL-97 [6], ORTEP-III [7]

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

Atom	Site	x	y	z	U_{iso}
H(2)	8*f*	0.3610(9)	0.020(1)	0.614(2)	0.071(6)
H(3)	8*f*	0.453(1)	–0.024(2)	0.582(3)	0.086(7)
H(4)	8*f*	0.460(1)	–0.147(2)	0.410(3)	0.097(7)
H(5)	8*f*	0.374(1)	–0.236(2)	0.294(3)	0.103(7)
H(6)	8*f*	0.2746(9)	–0.185(1)	0.340(2)	0.072(6)
H(8A)	8*f*	0.2859(8)	0.090(1)	0.377(2)	0.076(6)
H(8B)	8*f*	0.2776(8)	0.165(1)	0.512(2)	0.068(5)
H(8C)	8*f*	0.2262(9)	0.156(1)	0.359(2)	0.067(5)
H(10A)	8*f*	0.044(1)	0.070(2)	0.694(2)	0.105(7)
H(10B)	8*f*	0.106(1)	0.102(2)	0.800(3)	0.102(8)
H(12A)	8*f*	0.005(1)	0.172(1)	0.479(2)	0.078(6)
H(12B)	8*f*	0.050(1)	0.221(2)	0.382(3)	0.117(9)
H(12C)	8*f*	0.046(1)	0.104(2)	0.397(3)	0.107(8)
H(13A)	8*f*	0.058(1)	0.270(2)	0.715(3)	0.098(7)
H(13B)	8*f*	0.127(1)	0.265(2)	0.760(3)	0.090(8)
H(13C)	8*f*	0.097(2)	0.320(2)	0.595(4)	0.17(2)

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*f*	0.12985(2)	−0.01381(4)	0.64259(6)	0.0569(3)	0.0708(3)	0.0745(3)	0.0088(2)	0.0305(2)	0.0239(2)
O(1)	8*f*	0.21096(6)	−0.11632(8)	0.5320(2)	0.0697(7)	0.0449(7)	0.102(1)	−0.0011(6)	0.0379(7)	0.0064(6)
N(1)	8*f*	0.22802(5)	0.04325(8)	0.5099(1)	0.0407(6)	0.0399(7)	0.0512(7)	0.0025(5)	0.0145(5)	0.0028(5)
N(2)	8*f*	0.15455(6)	0.15671(9)	0.5437(2)	0.0450(7)	0.0496(8)	0.0612(8)	0.0053(6)	0.0167(6)	−0.0051(6)
C(1)	8*f*	0.30845(7)	−0.0750(1)	0.4791(2)	0.0505(9)	0.0405(9)	0.0559(9)	0.0070(7)	0.0149(7)	0.0067(7)
C(2)	8*f*	0.36167(8)	−0.0276(1)	0.5517(2)	0.054(1)	0.056(1)	0.077(1)	0.0053(8)	0.0099(9)	−0.002(1)
C(3)	8*f*	0.41900(9)	−0.0568(2)	0.5270(3)	0.049(1)	0.077(2)	0.110(2)	0.003(1)	0.011(1)	0.014(1)
C(4)	8*f*	0.4230(1)	−0.1321(2)	0.4296(3)	0.068(1)	0.073(2)	0.122(2)	0.031(1)	0.043(1)	0.027(1)
C(5)	8*f*	0.3706(1)	−0.1808(2)	0.3597(3)	0.085(2)	0.058(1)	0.107(2)	0.019(1)	0.043(1)	0.001(1)
C(6)	8*f*	0.31318(9)	−0.1534(1)	0.3851(2)	0.066(1)	0.049(1)	0.073(1)	0.0075(8)	0.022(1)	−0.0006(8)
C(7)	8*f*	0.24526(7)	−0.0520(1)	0.5083(2)	0.0497(8)	0.0433(9)	0.0504(9)	0.0009(7)	0.0133(7)	0.0020(7)
C(8)	8*f*	0.25766(8)	0.1193(1)	0.4347(2)	0.0502(9)	0.0431(9)	0.071(1)	0.0014(8)	0.0234(9)	0.0049(8)
C(9)	8*f*	0.17338(6)	0.0705(1)	0.5584(2)	0.0395(7)	0.0499(9)	0.0383(7)	0.0001(7)	0.0050(6)	−0.0008(6)
C(10)	8*f*	0.0877(1)	0.0863(2)	0.7012(3)	0.063(1)	0.103(2)	0.067(1)	0.023(1)	0.031(1)	0.017(1)
C(11)	8*f*	0.09450(7)	0.1693(1)	0.5928(2)	0.0451(9)	0.062(1)	0.056(1)	0.0069(7)	0.0150(7)	−0.0050(8)
C(12)	8*f*	0.0432(1)	0.1649(2)	0.4477(3)	0.054(1)	0.093(2)	0.073(1)	0.021(1)	0.008(1)	0.007(1)
C(13)	8*f*	0.0946(1)	0.2660(2)	0.6726(4)	0.071(2)	0.097(2)	0.124(2)	0.008(1)	0.035(2)	−0.046(2)

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