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Crystal structure of *N*-phenyl-3-[2-(4′-chlorophenylthio)propanoyl]-2-azetidinone, $C_{18}H_{16}ClNO_2S$

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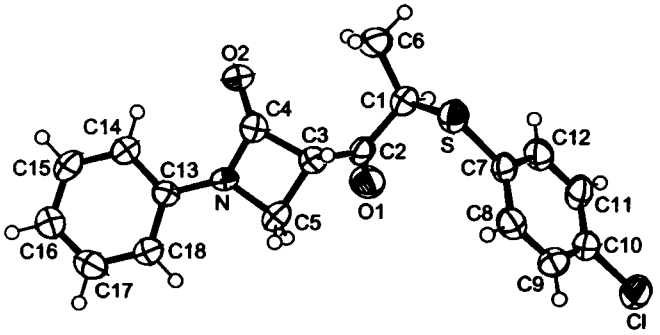

Abstract

$C_{18}H_{16}ClNO_2S$, monoclinic, $P12_1/c1$ (no. 14), a = 10.211(1) Å, b = 6.5258(9) Å, c = 24.334(3) Å, β = 90.279(9)°, V = 1621.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.044, $wR_{ref}(F^2)$ = 0.112, T = 293 K.

Source of material

To a solution of *N,O*-dimethylhydroxylamine hydrochloride (2.00 g, 20.70 mmol) and pyridine (3.30 ml, 41.16 mmol) in 15.0 mL acetonitrile, at 273 K, a solution of 2-(4′-chlorophenylthio)propanoyl chloride [1] (4.84 g, 20.58 mmol) in 5 mL acetonitrile was added slowly. The reaction mixture was allowed to reach room temperature and was stirred overnight. Then it was concentrated and poured into 0.2 N HCl (10.0 mL) solution, washed with water and three times extracted with chloroform. The combined extracts were dried over $MgSO_4$. After solvent evaporation the crude material was purified by chromatography on silica gel (chloroform), giving a viscous liquid of 2-(4′-chlorophenylthio)-*N*-methoxy-*N*-methylpropanamide (3.93 g, 14.40 mmol, 70 % yield). A solution of *n*-butyllithium (3.00 mL, 1.9 M in *n*-hexane) was added to isopropylamine (0.80 mL, 5.47 mmol) in THF (6.6 mL) at 195 K. It was then added a solution of *N*-phenyl-2-azetidinone (0.80 g, 5.47 mmol) in THF (4.6 mL) and stirred for 30 minutes at the same temperature. Then, a solution of 1.19 g (4.56 mmol) of 2-(4′-chlorophenylthio)-*N*-methoxy-*N*-methylpropanamide in THF (2.0 mL) was added slowly. The reaction was monitored by TLC with chloroform/*n*-hexane (70 : 30) as eluent. The reaction mixture was poured into aqueous NH_4Cl and extracted with chloroform (3×). The combined extracts were dried over $MgSO_4$. After solvent evaporation, the obtained amorphous white solid was recrystallized from methanol giving 1.30 g of the C1(*R*)C3(S)/C1(*S*)C3(*R*) diastereomer of the title compound (2.05 mmol, yield 45 %; m.p. 384-386 K). Crystals for X-ray analysis were obtained by vapor diffusion from chloroform/*n*-hexane at 278 K.

Elemental analysis: found – C, 62.73 %; H, 4.88 %; N, 4.37 %; calc. for $C_{18}H_{16}ClNO_2S$ – C, 62.51 %; H, 4.66 %; N, 4.05 %.

Experimental details

Due to the poor diffraction quality of the crystal, the number of observed reflections was low. H atoms were geometrically fixed to their parent ones and their displacement parameters calculated as $1.2U_{eq}$(C) or $1.5U_{eq}$(C).

Discussion

The four-membered ring is planar within experimental accuracy (r.m.s. being 0.006 Å) and makes a dihedral angle of 6.6(3)° with the phenyl ring attached to it, which can be ascribed to the short C···O interaction: d(C14···O2) = 3.114(6) Å, d(H14···O2) = 2.51 Å, ∠C14–H14···O2 = 123°. In turn the phenyl rings make a dihedral angle of 52.6(1)° to each other. Bond distances and angles in the four-membered ring are in the expected range (d(N—C4) = 1.356(6) Å (1.348 Å), d(N—C5) = 1.465(5) Å (1.472 Å), d(C3—C4) = 1.549(6) Å (1.548 Å), d(C3—C5) = 1.538(6) Å (1.561 Å), d(C—O) = 1.207(6) Å (1.218 Å), ∠C4–N–C5 = 95.5(4)° (95.90°), ∠C3–C4–N = 91.5(4)° (91.13°)). The numbers in parentheses correspond to the mean values of eighteen structures with such a ring, found in the CSD [2]. The molecules are arranged via C–H···O hydrogen bonds, first they are related in an helical fashion through (d(C1···O1^{i}) = 3.471(6) Å, ∠C1–H1···O1^{i} = 152°). The helices are connected through C18–H18···O2^{ii} bond (d(C18···O2^{ii}) = 3.442(6) Å, ∠C18–H18···O2^{ii} = 177° (symmetry operations i: $-x,y+½,-z+¾$, ii: $x,y-1,z$).

Table 1. Data collection and handling.

Crystal:	colorless irregular plate, size 0.04 × 0.12 × 0.14 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.73 cm^{-1}
Diffractometer, scan mode:	Nonius CAD4, $\theta/2\theta$
$2\theta_{max}$:	48.38°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5194, 2599
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1047
$N(param)_{refined}$:	209
Programs:	SIR92 [3], SHELXL-97 [4], PARST95 [5], PLATON [6], WinGX [7], ORTEP-3 [8]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4e	−0.0780	0.5216	0.7226	0.061
H(3)	4e	−0.1075	0.3151	0.5834	0.051
H(5A)	4e	0.1002	0.0388	0.6040	0.063
H(5B)	4e	−0.0023	0.0255	0.5541	0.063
H(6A)	4e	0.0088	0.7504	0.6555	0.099
H(6B)	4e	−0.1302	0.8165	0.6760	0.099
H(6C)	4e	−0.1151	0.7079	0.6189	0.099
H(8)	4e	−0.3525	0.0237	0.6803	0.058
H(9)	4e	−0.4007	−0.2085	0.7485	0.057
H(11)	4e	−0.2879	0.1978	0.8627	0.063
H(12)	4e	−0.2429	0.4320	0.7944	0.062
H(14)	4e	0.2916	0.5050	0.4937	0.062
H(15)	4e	0.4541	0.4301	0.4315	0.067
H(16)	4e	0.4965	0.0956	0.4060	0.069
H(17)	4e	0.3742	−0.1647	0.4444	0.075
H(18)	4e	0.2158	−0.0960	0.5083	0.057

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}
Cl	4e	−0.3807(1)	−0.2021(2)	0.86313(5)	0.066(1)	0.065(1)	0.065(1)	−0.0007(8)	0.0123(7)	0.0143(8)
S	4e	−0.2714(1)	0.4337(2)	0.67655(5)	0.0466(8)	0.056(1)	0.058(1)	0.0004(8)	0.0092(7)	0.0052(8)
N	4e	0.1353(4)	0.2528(6)	0.5436(2)	0.054(3)	0.026(3)	0.047(2)	0.005(2)	0.012(2)	0.006(2)
O(1)	4e	0.0500(3)	0.2326(6)	0.6889(1)	0.075(3)	0.062(3)	0.060(2)	0.018(2)	0.001(2)	0.009(2)
O(2)	4e	0.1010(4)	0.6066(6)	0.5525(1)	0.095(3)	0.033(2)	0.073(3)	0.004(2)	0.034(2)	0.006(2)
C(1)	4e	−0.0992(4)	0.5077(7)	0.6834(2)	0.050(3)	0.045(3)	0.058(3)	−0.006(3)	0.014(3)	0.003(3)
C(2)	4e	−0.0154(4)	0.3387(8)	0.6593(2)	0.032(3)	0.041(3)	0.054(4)	−0.006(3)	0.009(3)	0.007(3)
C(3)	4e	−0.0181(4)	0.3062(7)	0.5979(2)	0.043(3)	0.037(3)	0.049(3)	0.000(3)	0.007(2)	0.001(3)
C(4)	4e	0.0791(5)	0.4282(9)	0.5618(2)	0.055(3)	0.044(4)	0.043(3)	0.002(3)	0.009(3)	0.002(3)
C(5)	4e	0.0528(5)	0.1151(7)	0.5760(2)	0.055(3)	0.043(4)	0.059(4)	−0.009(3)	0.015(3)	0.008(3)
C(6)	4e	−0.0824(5)	0.7147(8)	0.6559(2)	0.058(4)	0.043(4)	0.097(4)	−0.005(3)	0.020(3)	0.000(3)
C(7)	4e	−0.2929(4)	0.2541(7)	0.7305(2)	0.031(3)	0.045(4)	0.047(3)	0.001(3)	0.008(2)	0.002(3)
C(8)	4e	−0.3401(4)	0.0594(8)	0.7170(2)	0.046(3)	0.052(4)	0.046(3)	0.002(3)	0.004(2)	−0.008(3)
C(9)	4e	−0.3683(4)	−0.0797(8)	0.7576(2)	0.047(3)	0.044(3)	0.052(4)	−0.005(3)	0.001(3)	−0.002(3)
C(10)	4e	−0.3484(4)	−0.0278(8)	0.8114(2)	0.042(3)	0.045(4)	0.049(4)	−0.001(3)	0.008(2)	0.002(3)
C(11)	4e	−0.3011(5)	0.1638(9)	0.8260(2)	0.055(3)	0.065(4)	0.038(3)	−0.013(3)	0.009(3)	−0.002(3)
C(12)	4e	−0.2742(4)	0.3027(8)	0.7850(2)	0.050(3)	0.054(4)	0.052(3)	−0.011(3)	0.007(3)	−0.017(3)
C(13)	4e	0.2346(5)	0.2107(8)	0.5061(2)	0.050(3)	0.033(3)	0.037(3)	−0.001(3)	0.004(2)	−0.003(3)
C(14)	4e	0.3080(5)	0.3698(7)	0.4837(2)	0.064(4)	0.040(4)	0.050(3)	−0.003(3)	0.013(3)	0.003(3)
C(15)	4e	0.4051(5)	0.3242(8)	0.4466(2)	0.057(4)	0.048(4)	0.062(4)	−0.012(3)	0.016(3)	0.011(3)
C(16)	4e	0.4312(5)	0.1249(8)	0.4313(2)	0.065(4)	0.053(4)	0.053(4)	−0.001(3)	0.013(3)	−0.004(3)
C(17)	4e	0.3581(5)	−0.0297(8)	0.4546(2)	0.070(4)	0.045(4)	0.071(4)	0.001(3)	0.016(3)	−0.012(3)
C(18)	4e	0.2621(5)	0.0109(7)	0.4922(2)	0.052(3)	0.038(3)	0.054(3)	−0.001(3)	0.008(3)	0.004(3)

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