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Crystal structure of *N*-methoxy-*N*-methyl-2-[(4′-nitrophenyl)sulfinyl]-propanamide, $C_{11}H_{14}N_2O_5S$

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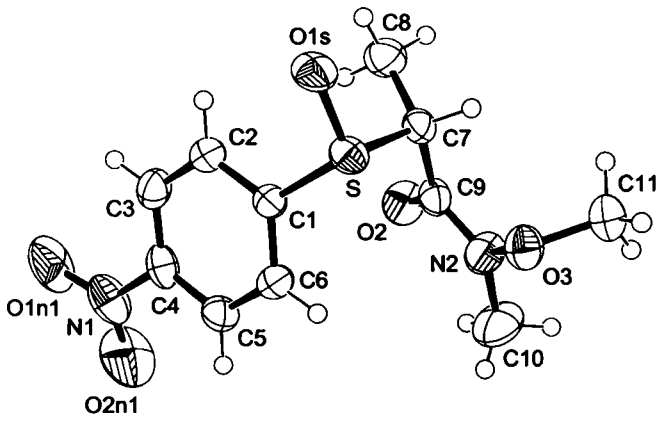

Abstract

$C_{11}H_{14}N_2O_5S$, monoclinic, $P12_1/c1$ (no. 14), a = 7.4329(9) Å, b = 23.631(3) Å, c = 7.900(1) Å, β = 110.723(8)°, V = 1297.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.045, $wR_{ref}(F^2)$ = 0.114, T = 293 K.

Source of material

A solution of 2-(4′-nitrophenylthio)propanoyl chloride (3.12 g, 14.53 mmol) in 5 ml CH_3CN was added slowly to a solution of *N,O*-dimethylhydroxylamine hydrochloride (1.42 g, 14,53 mmol) and pyridine (2.52 g, 31.96 mmol) in 10 ml CH_3CN at 273 K. The reaction mixture was allowed to reach room temperature and stirred overnight. The crude mixture was concentrated and poured into 0.2 N HCl (10.0 mL) solution, water (10.0 mL) and three times extracted with chloroform. The combined extracts were dried over $MgSO_4$ and rotary-evaporated. The crude material was purified by chromatography on silica gel (chloroform), affording *N*-methoxy-*N*-methyl-2-(4′-nitrophenylthio)propanamide as a viscous yellow liquid in 81 % yield (2.80 g, 11.76 mmol). The 2-(4′-nitrophenylthio)propanoyl chloride was obtained from the reaction of thionyl chloride and 2-(4′-nitrophenylthiophenyl)propionic acid, which in turn was obtained from the reaction of chloropropionic acid and 4-nitrothiophenol in aqueous solution of sodium hydroxide [1]. A solution of oxone (0.60 g, 0.98 mmol) in 4.2 mL of water was added slowly to a solution of *N*-methoxy-*N*-methyl-2-[(4′-nitrophenyl)thio]propanamide (0.37 g, 1.37 mmol) and $NaHCO_3$ (0.68 g, 8.14 mmol) in 3.2 mL acetone at 273 K. The reaction mixture was stirred for 30 minutes, and then poured into water and extracted with chloroform three times. The combined extracts were dried over $MgSO_4$ and rotary-evaporated. The crude material was purified by chromatography on silica gel (eluent gradient: chloroform/acetone 100:0 to 90:100) giving 0.23 g of *N*-methoxy-*N*-methyl-2-[(4′-nitrophenyl)sulfinyl]propanamide (0.80 mmol, 58 % yield) (a pair of diastereomers). The obtained amorphous yellow solid was fractionally recrystallized from chloroform/*n*-hexane affording initially the C(*R*)S(*S*)/C(*S*)S(*R*) diastereomer (m.p. 367-370 K, cf. stereogenic centers C7 and S) followed by the C(*R*)S(*R*)/C(*S*)S(*S*) diastereomer (m.p. 390-392 K) in the ratio of 8:2. Suitable crystals of the title compound (C(*R*)S(*R*)/C(*S*)S(*S*) diastereomer) were obtained by vapor diffusion from chloroform/*n*-hexane at 278 K.
Elemental analysis: found – C, 45.92 %; H, 4.94 %; N, 9.37 %; calc. for $C_{11}H_{14}N_2O_5S$ – C, 46.15 %; H, 4.93 %; N, 9.78 %.

Discussion

The S=O distance of 1.490(2) Å is the shortest distance found in the CSD [2] when searched for 1-(*C*-sulfinyl)-4-nitrobenzene, albeit the C–S–C angle of 98.0(1)° is the larger. The phenyl ring and the nitro moiety make an angle of 16.0(6)°. The molecules are arranged via C–H···O hydrogen bonds in the threedimensional framework. First, the molecules form centrosymmetric dimers (d(C7···O1S^{i}) = 3.381(4) Å, ∠C7–H7···O1S^{i} = 154°; d(C11···O1S^{i}) = 3.401 Å, ∠C11–H11C···O1S = 153°) giving rise to three eight membered rings. These are related in an helical fashion through interactions with d(C5···O2N1^{ii}) = 3.236(5) Å, ∠C5–H5···O2N1^{ii} = 140° and d(C10···O2^{ii}) = 3.371(5) Å, ∠C10–H10C···O2^{ii} = 130°. The helices are connected with d(C6···O1N1^{iii}) = 3.478(5) Å, ∠C6–H6···O1N1 = 142° (symmetry operations i: 2–x,–y,–z; ii: x,½–y,–½+z; iii: x,y,z–1).

Table 1. Data collection and handling.

Crystal:	colorless irregular plate, size 0.05 × 0.12 × 0.15 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.68 cm^{-1}
Diffractometer, scan mode:	Nonius CAD4, $\theta/2\theta$
$2\theta_{max}$:	51.16°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2615, 2433
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1349
$N(param)_{refined}$:	175
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(2)	4e	0.6852	0.0174	0.3629	0.047
H(3)	4e	0.5868	0.0635	0.5743	0.054
H(5)	4e	0.4586	0.2017	0.2579	0.052
H(6)	4e	0.5561	0.1546	0.0458	0.047
H(7)	4e	1.0303	0.0603	0.0297	0.045
H(8A)	4e	1.2144	0.0419	0.3162	0.077
H(8B)	4e	1.0409	0.0001	0.2779	0.077
H(8C)	4e	1.0486	0.0555	0.3893	0.077
H(10A)	4e	0.9570	0.2408	0.1096	0.117
H(10B)	4e	0.8054	0.2380	−0.0875	0.117
H(10C)	4e	1.0251	0.2426	−0.0568	0.117
H(11A)	4e	1.1127	0.1756	−0.2248	0.090
H(11B)	4e	1.0155	0.1267	−0.3605	0.090
H(11C)	4e	1.1517	0.1123	−0.1629	0.090

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	4e	0.7149(1)	0.04773(3)	0.0256(1)	0.0389(5)	0.0356(5)	0.0384(4)	0.0003(4)	0.0140(4)	−0.0073(4)
N(1)	4e	0.4552(5)	0.1667(2)	0.5668(5)	0.052(2)	0.088(3)	0.055(2)	−0.001(2)	0.025(2)	−0.023(2)
N(2)	4e	0.9467(5)	0.1659(1)	−0.0072(4)	0.076(2)	0.037(2)	0.048(2)	−0.002(2)	0.031(2)	−0.005(2)
O(1S)	4e	0.7228(3)	−0.01399(9)	0.0663(3)	0.050(2)	0.029(1)	0.073(2)	−0.003(1)	0.026(1)	−0.010(1)
O(1N1)	4e	0.4268(4)	0.1381(2)	0.6842(4)	0.081(2)	0.154(3)	0.052(2)	0.028(2)	0.043(2)	0.006(2)
O(2N1)	4e	0.4397(5)	0.2176(2)	0.5547(5)	0.122(3)	0.081(2)	0.116(3)	−0.006(2)	0.068(2)	−0.051(2)
O(2)	4e	1.0290(4)	0.1565(1)	0.2904(3)	0.073(2)	0.047(2)	0.047(2)	−0.009(1)	0.024(1)	−0.015(1)
O(3)	4e	0.8943(3)	0.1396(1)	−0.1765(3)	0.051(2)	0.055(2)	0.042(1)	−0.002(1)	0.020(1)	−0.003(1)
C(1)	4e	0.6344(4)	0.0825(1)	0.1884(4)	0.030(2)	0.029(2)	0.036(2)	−0.002(1)	0.012(2)	−0.003(2)
C(2)	4e	0.6412(5)	0.0545(1)	0.3432(4)	0.042(2)	0.037(2)	0.041(2)	0.004(2)	0.017(2)	0.005(2)
C(3)	4e	0.5826(5)	0.0816(2)	0.4685(5)	0.043(2)	0.056(2)	0.037(2)	−0.002(2)	0.015(2)	0.009(2)
C(4)	4e	0.5173(5)	0.1364(2)	0.4328(5)	0.039(2)	0.056(2)	0.039(2)	−0.009(2)	0.020(2)	−0.014(2)
C(5)	4e	0.5050(5)	0.1648(1)	0.2782(5)	0.047(2)	0.033(2)	0.055(2)	0.003(2)	0.025(2)	−0.004(2)
C(6)	4e	0.5640(5)	0.1368(1)	0.1532(4)	0.044(2)	0.035(2)	0.040(2)	0.002(2)	0.016(2)	0.005(2)
C(7)	4e	0.9714(5)	0.0705(1)	0.1186(4)	0.040(2)	0.033(2)	0.045(2)	0.001(2)	0.022(2)	−0.003(2)
C(8)	4e	1.0786(5)	0.0392(2)	0.2911(5)	0.040(2)	0.052(2)	0.057(2)	0.003(2)	0.012(2)	0.006(2)
C(9)	4e	0.9863(5)	0.1342(1)	0.1422(5)	0.038(2)	0.037(2)	0.045(2)	−0.005(2)	0.021(2)	−0.005(2)
C(10)	4e	0.9323(7)	0.2270(2)	−0.0108(6)	0.124(4)	0.035(2)	0.086(3)	0.004(2)	0.052(3)	0.004(2)
C(11)	4e	1.0572(6)	0.1385(2)	−0.2362(5)	0.069(3)	0.065(3)	0.062(3)	0.009(2)	0.042(2)	0.007(2)

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