Crystal structure of 2-phenylsulfinyl-cyclohexanone, $C_{12}H_{14}O_2S$

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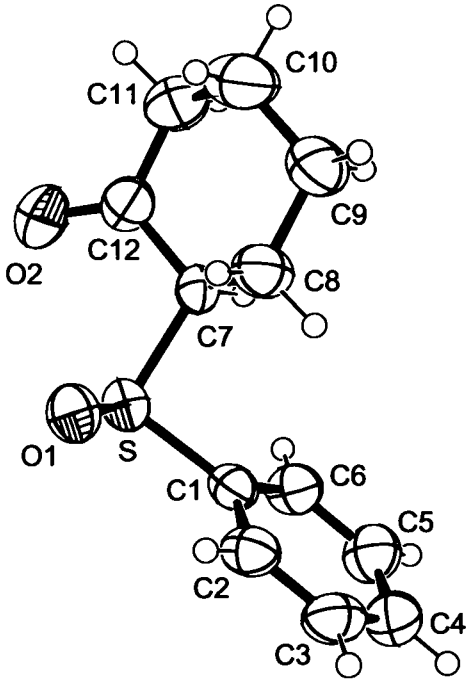

Abstract

$C_{12}H_{14}O_2S$, monoclinic, $P12_1/a1$ (no. 14), a = 10.787(1) Å, b = 10.3955(9) Å, c = 10.888(1) Å, β = 108.928(5)°, V = 1154.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.047, $wR_{ref}(F^2)$ = 0.142, T = 293 K.

Source of material

The starting 2-phenylsulfanyl-cyclohexanone was prepared from the reaction of 2-chloro-cyclohexanone and thiophenol [1]. A solution of SeO_2 (0.2 g, 1.8 mmol) and 30 % aqueous solution of H_2O_2 (0.8 mL, 7.27 mmol) in CH_3OH (5 mL) was added dropwise, at 273 K, to a solution of 2-phenylsulfanylcyclohexanone (1.5 g, 7.27 mmol) in CH_3OH (10 mL) [2]. The reaction mixture was stirred at 273 K for 3 hours and at room temperature for 2 hours. After completion of the reaction a saturated aqueous NaCl solution (40 mL) was added, the aqueous layer was extracted with CH_2Cl_2 (60 mL) and the organic solution was dried over anhydrous $MgSO_4$. After solvent evaporation under reduced pressure 1.2 g (5.39 mmol, yield 74 %; m.p. 364-367 K) of the crude 2-phenylsulfinyl-cyclohexanone was obtained (m.p. 377-378 K [3]). The oxidation afforded a mixture of 2:1 [C(*R*)S(*S*)/C(*S*)S(*R*)] and [C(*R*)S(*R*)/C(*S*)S(*S*)] diastereomeric sulfoxides, respectively, (cf. stereogenic centers C2 and S) determined from ^{1}H NMR spectra of the crude product. From *n*-hexane/acetone fractional crystallization the pure [C(*R*)S(*S*)/C(*S*)S(*R*)] diastereomer was obtained as a white solid (m.p. 366-367 K). Suitable crystals for X-ray analysis of the referred diastereomer were obtained by vapor diffusion from *n*-hexane/acetone at 298 K.

Elemental analysis – found: C, 64.48 %; H, 6.26 %; calc. for $C_{12}H_{14}O_2S$: C, 64.83 %; H, 6.35 %.

Discussion

The cyclohexanone ring is in a slightly distorted chair conformation, the Cremer and Pople's [4] ring-puckering parameters being: q_2 = 0.0603(4) Å, q_3 = 0.530(5) Å, φ_2 = 117(4)°, θ_2 = 6.5(4)° and Q = 0.533(5) Å. The dihedral angle between the phenyl ring and the OSC_{ph} moiety amounts of 4.7(3)° and that of 4-*t*-butyl-2-(ptolylsulfinyl)cyclohexanone [5] (CSD ref code HAFCEW) is 0.98°. The S=O distance of 1.497(3) Å is in the range found in the CSD [6], mean of 1.4875 Å. The molecules are arranged via C–H···O hydrogen bonds in a threedimensional framework. First the molecules form centrosymmetric dimers: d(C3···O1^i) = 3.387(5) Å, ∠C3–H3···O1^i = 131°, giving rise to a twelve-membered ring. They are, in turn, related in an helical fashion through: d(C7···O1^{ii}) = 3.271(4) Å, ∠C7–H7···O1^{ii} = 163°; d(C11···O2^{ii}) = 3.586(6) Å, ∠C11–H11B···O2^{ii} = 152° (symmetry operations: i: 1–x,1–y,–z; ii: x–½,½–y,z).

Table 1. Data collection and handling.

Crystal:	colorless irregular plate, size 0.08 × 0.10 × 0.12 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.58 cm^{-1}
Diffractometer, scan mode:	Nonius CAD4, $\theta/2\theta$
$2\theta_{max}$:	50.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2251, 2136
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 985
$N(param)_{refined}$:	136
Programs:	SIR92 [7], SHELXL-97 [8], PARST [9], PLATON [10], ORTEP-3 [11], WinGX [12]

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

Atom	Site	x	y	z	U_{iso}
H(2)	4*e*	0.4219	0.4247	–0.0490	0.064
H(3)	4*e*	0.2883	0.4873	–0.2525	0.072
H(4)	4*e*	0.0846	0.3968	–0.3414	0.077
H(5)	4*e*	0.0105	0.2461	–0.2249	0.077
H(6)	4*e*	0.1413	0.1860	–0.0195	0.066
H(7)	4*e*	0.2140	0.2793	0.1976	0.050

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(8A)	4e	0.2451	0.4854	0.1352	0.075
H(8B)	4e	0.3771	0.4991	0.2506	0.075
H(9A)	4e	0.2113	0.6054	0.3059	0.085
H(9B)	4e	0.1258	0.4799	0.2802	0.085

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(10A)	4e	0.2253	0.5043	0.5007	0.104
H(10B)	4e	0.3638	0.5117	0.4829	0.104
H(11A)	4e	0.3400	0.3052	0.5514	0.092
H(11B)	4e	0.2037	0.2894	0.4429	0.092

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	0.40130(9)	0.2501(1)	0.14203(9)	0.0436(5)	0.0554(6)	0.0524(6)	0.0081(6)	0.0155(4)	0.0024(6)
O(1)	4e	0.5209(2)	0.3328(3)	0.1711(2)	0.037(1)	0.095(2)	0.062(2)	-0.002(2)	0.015(1)	0.000(2)
O(2)	4e	0.4449(3)	0.1942(3)	0.4092(3)	0.081(2)	0.085(2)	0.061(2)	0.025(2)	0.012(2)	0.018(2)
C(1)	4e	0.2946(3)	0.2994(3)	-0.0151(3)	0.043(2)	0.046(2)	0.046(2)	0.002(2)	0.019(2)	-0.006(2)
C(2)	4e	0.3388(4)	0.3891(4)	-0.0842(4)	0.050(2)	0.063(3)	0.050(2)	-0.007(2)	0.022(2)	-0.006(2)
C(3)	4e	0.2592(4)	0.4260(4)	-0.2061(4)	0.076(3)	0.058(3)	0.052(3)	0.000(2)	0.031(2)	0.005(2)
C(4)	4e	0.1376(4)	0.3726(4)	-0.2588(4)	0.068(3)	0.070(3)	0.051(3)	0.011(2)	0.015(2)	-0.004(2)
C(5)	4e	0.0932(4)	0.2822(4)	-0.1890(4)	0.052(2)	0.076(4)	0.061(3)	-0.008(2)	0.011(2)	-0.003(2)
C(6)	4e	0.1713(3)	0.2459(4)	-0.0668(3)	0.052(2)	0.061(2)	0.051(2)	-0.007(2)	0.017(2)	-0.002(2)
C(7)	4e	0.3024(3)	0.3151(3)	0.2344(3)	0.034(2)	0.046(2)	0.042(2)	0.002(2)	0.010(2)	0.001(2)
C(8)	4e	0.2903(4)	0.4610(4)	0.2246(4)	0.084(3)	0.054(3)	0.059(3)	0.014(2)	0.036(2)	0.008(2)
C(9)	4e	0.2150(4)	0.5122(4)	0.3112(4)	0.085(3)	0.062(3)	0.071(3)	0.016(2)	0.033(3)	-0.001(2)
C(10)	4e	0.2776(5)	0.4729(5)	0.4493(5)	0.106(4)	0.096(4)	0.068(3)	0.006(3)	0.041(3)	-0.014(3)
C(11)	4e	0.2903(5)	0.3268(5)	0.4624(4)	0.090(3)	0.092(4)	0.055(3)	0.013(3)	0.032(2)	0.016(3)
C(12)	4e	0.3565(4)	0.2699(4)	0.3739(4)	0.050(2)	0.061(3)	0.052(3)	-0.002(2)	0.015(2)	0.005(2)

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