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Crystal structure of *cis*-4-*tert*-butyl-2-(4-nitrophenylsulfonyl)cyclohexanone, $C_{16}H_{21}NO_5S$

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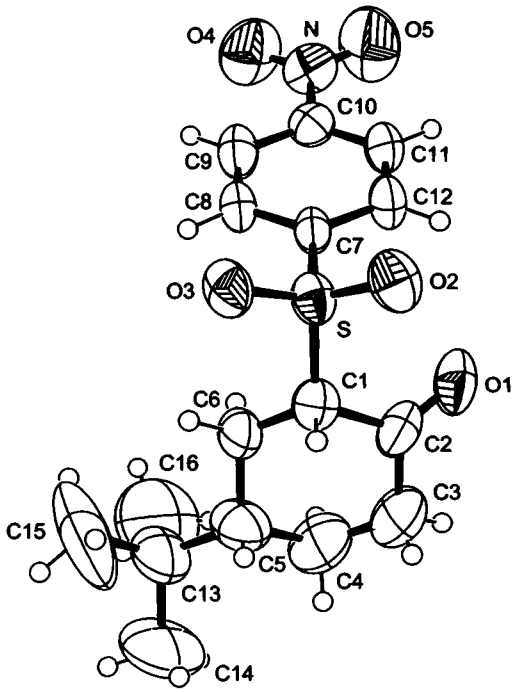

Abstract

$C_{16}H_{21}NO_5S$, triclinic, $P\bar{1}$ (no. 2), a = 7.3395(9) Å, b = 11.103(1) Å, c = 11.391(1) Å, α = 107.933(9)°, β = 95.12(1)°, γ = 99.96(1)°, V = 859.8 Å^3, Z = 2, $R_{gt}(F)$ = 0.062, $wR_{ref}(F^2)$ = 0.218, T = 293 K.

Source of material

Firstly, the 4-*tert*-butyl-2-(4-nitrophenylsulfanyl)cyclohexanone was obtained from the reaction of 2-bromo-4-*tert*-butyl-cyclohexanone and 4-nitrobenzenethiol [1], then to a solution of the product (2.0 g, 6.5 mmol) in methanol (10 mL) and CH_2Cl_2 (3 mL) at 273 K was added slowly a solution of hydrogen peroxide (30 %, 3.7 mL, 32.5 mmol) and selenium dioxide (0.72 g, 6.5 mmol) in methanol [2]. After stirring for 5 h, a saturated aqueous NaCl solution (40 mL) was added and the crude product was extracted with CH_2Cl_2 (3 x 30 mL). The organic layer was dried over anhydrous $MgSO_4$. The solvent was removed and the amorphous yellow solid was recrystallized from ethanol giving 1.61 g of the title compound (4.74 mmol, 72 % yield, m.p. 405-406 K). Crystals were obtained by slow evaporation from anhydrous ethanol at 298 K. Elemental analysis: found – C, 56.23 %; H, 6.03 %; N, 3.99 %; calc. for $C_{16}H_{21}NO_5S$ – C, 56.62 %; H, 6.24 %; N, 4.13 %.

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Experimental details

The high U_{ii} values for C14 – C16 can be ascribed to the rotational disorder of the *tert*-butyl group.

Discussion

The cyclohexanone ring is in a slightly distorted chair conformation, the Cremer and Pople's ring-puckering [3] parameters being: q_2 = 0.0715(6) Å, q_3 = 0.482(5) Å, φ_2 = –103(5)°, θ_2 = 8.4(7)° and Q = 0.487(5) Å. The molecules are arranged via C–H···O hydrogen bonds: d(C1···O2^{i}) = 3.442(5) Å, ∠C1–H1···O1^{i} = 156°; d(C11···O1^{ii}) = 3.267(5) Å, ∠C11–H11···O1^{ii} = 177°; d(C9–H9···O1^{iii}) = 3.262(6) Å, ∠C9–H9···O1^{iii} = 126° (symmetry operations i: $-x+2,-y,-z$; ii: $-x+2,-y,-z+1$; iii: $x-1,y,z$).

Table 1. Data collection and handling.

Crystal:	yellowish, irregular, size 0.05 x 0.10 x 0.15 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.12 cm^{-1}
Diffractometer, scan mode:	Nonius CAD4, $\theta/2\theta$
$2\theta_{max}$:	51.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3533, 3352
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1564
$N(param)_{refined}$:	211
Programs:	SIR92 [3], SHELXL-97 [4], PARST95 [5], PLATON [6], WinGX [7], ORTEP-3 [8]

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

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	0.9870	0.1287	0.1054	0.077
H(3A)	2*i*	1.2181	0.3325	0.4038	0.153
H(3B)	2*i*	1.2444	0.3093	0.2644	0.153
H(4A)	2*i*	1.1018	0.4747	0.3197	0.148
H(4B)	2*i*	0.9550	0.4012	0.3790	0.148
H(5)	2*i*	0.9690	0.3408	0.1236	0.108
H(6A)	2*i*	0.7085	0.2098	0.2307	0.096
H(6B)	2*i*	0.7098	0.1779	0.0870	0.096
H(8)	2*i*	0.4366	–0.0421	0.1467	0.068
H(9)	2*i*	0.2373	–0.1089	0.2730	0.083
H(11)	2*i*	0.6720	–0.1793	0.4613	0.077
H(12)	2*i*	0.8681	–0.1143	0.3344	0.076
H(14A)	2*i*	0.9753	0.5536	0.1306	0.252
H(14B)	2*i*	0.9346	0.6159	0.2665	0.252
H(14C)	2*i*	0.7995	0.6156	0.1518	0.252
H(15A)	2*i*	0.5318	0.3249	0.0612	0.469
H(15B)	2*i*	0.7070	0.3371	–0.0069	0.469
H(15C)	2*i*	0.6026	0.4520	0.0310	0.469
H(16A)	2*i*	0.6120	0.5451	0.2887	0.342
H(16B)	2*i*	0.7330	0.4764	0.3573	0.342
H(16C)	2*i*	0.5488	0.3965	0.2662	0.342

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	2*i*	0.8084(1)	−0.04582(9)	0.11682(8)	0.0631(7)	0.0596(6)	0.0467(5)	0.0212(5)	0.0026(4)	0.0155(4)
N	2*i*	0.3158(6)	−0.1965(4)	0.4552(4)	0.080(3)	0.084(3)	0.070(2)	0.009(2)	0.015(2)	0.022(2)
O(1)	2*i*	1.0929(5)	0.0979(4)	0.3450(3)	0.072(2)	0.114(3)	0.080(2)	0.026(2)	−0.022(2)	0.029(2)
O(2)	2*i*	0.9538(4)	−0.1191(3)	0.1117(2)	0.078(2)	0.080(2)	0.071(2)	0.040(2)	0.023(2)	0.025(1)
O(3)	2*i*	0.6861(4)	−0.0683(3)	0.0024(2)	0.089(2)	0.070(2)	0.042(1)	0.018(2)	−0.006(1)	0.017(1)
O(4)	2*i*	0.1544(6)	−0.1896(5)	0.4428(4)	0.084(3)	0.160(4)	0.126(3)	0.024(3)	0.039(2)	0.058(3)
O(5)	2*i*	0.3784(7)	−0.2358(6)	0.5317(5)	0.120(3)	0.227(5)	0.143(4)	0.036(4)	0.041(3)	0.133(4)
C(1)	2*i*	0.9116(6)	0.1208(4)	0.1705(4)	0.061(3)	0.070(3)	0.060(2)	0.015(2)	0.003(2)	0.021(2)
C(2)	2*i*	1.0599(6)	0.1656(5)	0.2870(4)	0.046(2)	0.084(3)	0.078(3)	0.008(2)	−0.007(2)	0.018(2)
C(3)	2*i*	1.1519(9)	0.3029(6)	0.3191(7)	0.092(4)	0.100(4)	0.159(6)	−0.018(4)	−0.053(4)	0.036(4)
C(4)	2*i*	1.0263(9)	0.3905(6)	0.3101(6)	0.114(5)	0.080(4)	0.129(5)	−0.020(3)	−0.044(4)	0.009(3)
C(5)	2*i*	0.8914(8)	0.3460(4)	0.1899(4)	0.119(4)	0.060(3)	0.081(3)	0.005(3)	−0.003(3)	0.021(2)
C(6)	2*i*	0.7891(7)	0.2093(4)	0.1676(4)	0.084(3)	0.058(2)	0.086(3)	0.003(2)	−0.032(2)	0.024(2)
C(7)	2*i*	0.6660(5)	−0.0782(3)	0.2251(3)	0.050(2)	0.047(2)	0.048(2)	0.018(2)	−0.006(2)	0.010(2)
C(8)	2*i*	0.4823(5)	−0.0721(4)	0.2088(3)	0.053(2)	0.067(2)	0.055(2)	0.021(2)	−0.002(2)	0.025(2)
C(9)	2*i*	0.3639(6)	−0.1104(4)	0.2840(4)	0.063(3)	0.077(3)	0.069(2)	0.029(2)	−0.001(2)	0.022(2)
C(10)	2*i*	0.4409(6)	−0.1513(3)	0.3766(3)	0.061(3)	0.053(2)	0.050(2)	0.010(2)	0.007(2)	0.010(2)
C(11)	2*i*	0.6251(6)	−0.1529(4)	0.3969(3)	0.064(3)	0.076(3)	0.056(2)	0.018(2)	−0.005(2)	0.030(2)
C(12)	2*i*	0.7409(6)	−0.1152(4)	0.3214(3)	0.058(2)	0.081(3)	0.058(2)	0.025(2)	−0.002(2)	0.032(2)
C(13)	2*i*	0.763(1)	0.4378(5)	0.1761(6)	0.145(6)	0.059(3)	0.125(5)	0.006(3)	−0.031(4)	0.031(3)
C(14)	2*i*	0.879(1)	0.5677(6)	0.1818(8)	0.221(9)	0.064(3)	0.211(8)	0.006(5)	0.009(7)	0.054(4)
C(15)	2*i*	0.640(2)	0.3832(8)	0.055(1)	0.49(2)	0.085(5)	0.28(1)	0.037(8)	−0.26(1)	0.042(6)
C(16)	2*i*	0.655(2)	0.466(1)	0.281(1)	0.173(9)	0.19(1)	0.37(2)	0.106(8)	0.08(1)	0.12(1)

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