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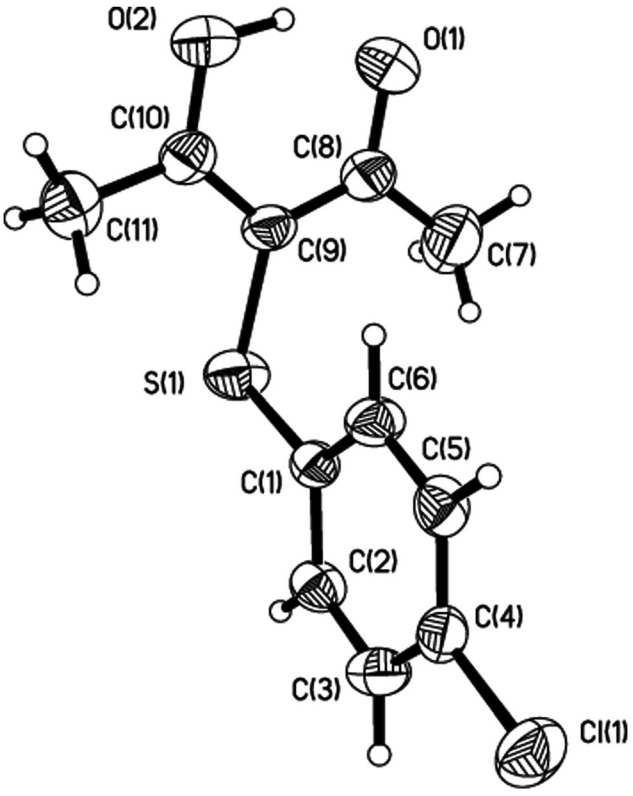
Crystal structure of (*E*)-3-((4-chlorophenyl)thio)-4-hydroxypent-3-en-2-one, $C_{11}H_{11}ClO_2S$



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Abstract

$C_{11}H_{11}ClO_2S$, orthorhombic, $P2_12_12_1$ (no. 19), a = 5.7516(7) Å, b = 7.4097(12) Å, c = 27.461(3) Å, V = 1170.3(3) Å^3, Z = 4, $R_{gt}(F)$ = 0.0564, $wR_{ref}(F^2)$ = 0.0990, T = 293 K.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.28 × 0.26 × 0.25 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.48 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	28.3°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	3371, 2238, 0.020
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 1609
$N(param)_{refined}$:	138
Programs:	CrysAlis^{PRO} [1], Olex2 [2], SHELX [3]

CCDC no.: 2208474

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

To a solution of acetylacetone (0.400 g, 4 mmol) and 4-chlorothiophenol (0.145 g, 1 mmol) in DMSO (1 mL) was added Na_2CO_3 (130 mg, 1 mmol). The mixture was stirred at 40 °C under oxygen atmosphere for 17 h. The mixture was then added to water (5 mL). The resulting mixture was extracted with ethylether (10 mL) for three times. The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. After removal of the solvent, the residue was then purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (25:1) to give the desired (204 mg, 84%) as a yellow solid. Single crystals suitable for X-ray diffraction were obtained by crystallization of the title compound from ethyl acetate. Melting point: 96 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ 17.27 (s, 1H), 7.24 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 2.32 (s, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 198.4, 136.4, 131.1, 129.4, 126.0, 101.3, 24.4.

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.3906 (3)	0.6267 (2)	0.82784 (4)	0.0921 (5)
S1	0.0846 (2)	0.7068 (2)	0.60946 (4)	0.0772 (5)
O1	0.3736 (8)	0.3114 (5)	0.53531 (13)	0.0967 (12)
O2	0.6005 (6)	0.5847 (5)	0.52127 (11)	0.0862 (11)
H2	0.5335	0.4519	0.5165	0.129*
C1	0.1823 (7)	0.6769 (6)	0.67022 (14)	0.0511 (11)
C2	0.0396 (7)	0.7395 (7)	0.70691 (16)	0.0593 (12)
H2A	−0.1016	0.7929	0.6988	0.071*
C3	0.1007 (8)	0.7251 (7)	0.75520 (16)	0.0684 (14)
H3	0.0026	0.7683	0.7795	0.082*
C4	0.3086 (8)	0.6458 (6)	0.76689 (15)	0.0570 (12)
C5	0.4532 (7)	0.5829 (6)	0.73148 (16)	0.0608 (13)
H5	0.5938	0.5294	0.7399	0.073*
C6	0.3906 (7)	0.5988 (6)	0.68296 (15)	0.0621 (13)
H6	0.4900	0.5563	0.6588	0.075*
C7	0.0489 (11)	0.2929 (9)	0.5870 (2)	0.107 (2)
H7A	−0.0946	0.3206	0.5708	0.161*
H7B	0.0364	0.3239	0.6208	0.161*
H7C	0.0809	0.1662	0.5839	0.161*
C8	0.2415 (9)	0.3982 (9)	0.56437 (17)	0.0718 (15)
C9	0.2799 (8)	0.5821 (8)	0.57347 (15)	0.0609 (13)
C10	0.4671 (9)	0.6699 (8)	0.55076 (16)	0.0629 (14)
C11	0.5252 (9)	0.8637 (7)	0.55787 (18)	0.0800 (17)
H11A	0.6802	0.8862	0.5464	0.120*
H11B	0.5154	0.8931	0.5919	0.120*
H11C	0.4174	0.9370	0.5399	0.120*

atoms with C–H = 0.96 Å (methyl), Uiso(H) = 1.5 Ueq(C), C–H = 0.93 Å (aromatic), Uiso(H) = 1.2 Ueq(C). Position of hydrogen atom of hydroxyl group was refined freely with Uiso(H) = 1.5 Ueq(O).

Comment

α-Thio-*β*-diketones are important organosulfur compounds in biochemistry and organic synthesis. They have significant biological activity [4, 5] in pharmaceuticals, such as many of the well-known antibiotics [6, 7]. What's more, *α*-thio-*β*-diketones have attracted much attention because they serve as important intermediates in heterocycle synthesis [8, 9], and they are useful synthons for the syntheses of a number of heterocyclic frameworks like coumarins and *α*-pyrones etc. [10]. Further, they are useful precursors for generating new quaternary chiral centers [11]. Meanwhile, this contribution is part of our continuing interest in synthesis, characterization and understanding of hydrogen bonding schemes of the delocalized enol form in the acetylacetone unite [12].

The asymmetric unit of the title complex contains one acetylacetone molecule and one 4-chlorothiophenol molecules. The single crystal analysis of the title compound has shown the acetylacetone and the 4-chlorothiophenol fragments are linked by carbonyl-sulfur bonds. The acetylacetone together with sulfur atom is almost strictly planar, whereby the largest deviation for the S1 atom from the acetylacetone plane is 0.140 Å. The dihedral angle between the acetylacetone group and 4-chlorothiophenol were found to be 89.02°. The C(1)–S(1)–C(9)–C(8) and C(1)–S(1)–C(9)–C(10) torsion angles are 87.5(4)° and −97.1(4)°. The C(1)–S(1)–C(9) bond angle is 105.1(2)°. Within the acetylacetone unit, the dimensions and planarity are consistent with their adoption of a localized enol form. The bond lengths of C(9)–C(10), C(9)–C(8) are 1.404(6) and 1.403(7) Å respectively. The only intramolecular O(2)–H(2)···O(1) hydrogen bond is observed. The H2···O1 distance is 1.48 Å. The O(1)···O(2) separation is 2.440(5) Å. The structure of the molecule is the same as in similar crystal structures like 1,3-bis(trimethylsilyloxy)-1,3-butadienes [13]. The bond lengths and angles are all in the expected ranges. And no unusual intermolecular contacts, were observed in this crystal.

The complete set of X-ray diffraction data for the title compound was deposited to the Cambridge Crystallographic Data Centre (CCDC entry no. 2208474).

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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