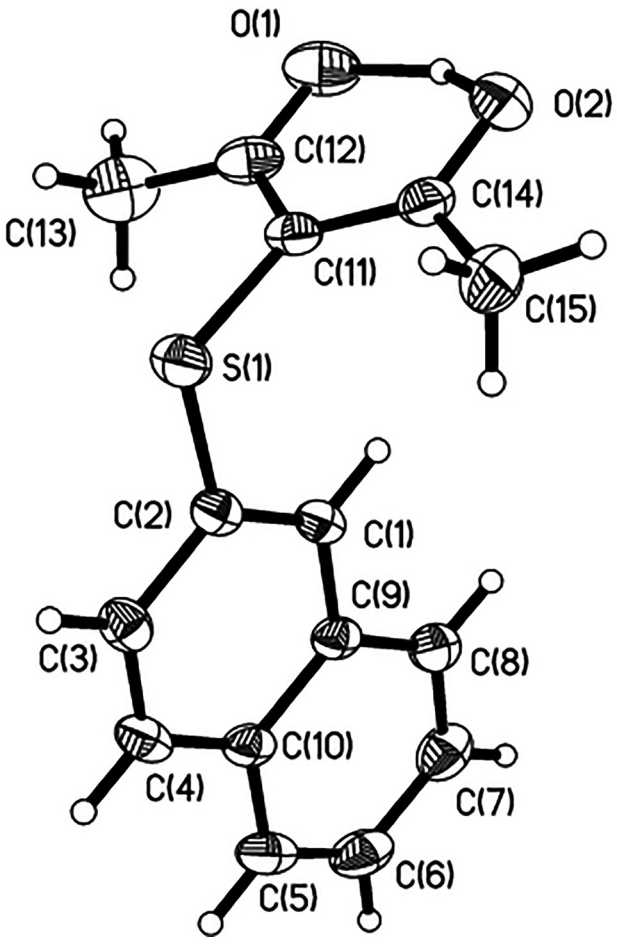
Ya-Xin Wen, Ya-Fei Guo*, Le Dong, Jun-Ying Ma and Bing-You Fan

Crystal structure of 4-Hydroxy-3-(naphthalen-2-ylthio)pent-3-en-2-one, $C_{15}H_{14}O_2S$



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***Corresponding author: Ya-Fei Guo**, School of Chemical Engineering and Pharmaceutics, Henan University of Science and Technology, Luoyang, Henan 471003, P. R. China, E-mail: guo.yafei@163.com. https://orcid.org/0000-0001-9953-021X
Ya-Xin Wen and Bing-You Fan, College of Agriculture, Henan University of Science and Technology, Luoyang, Henan 471003, P. R. China
Le Dong, School of Chemical Engineering and Pharmaceutics, Henan University of Science and Technology, Luoyang, Henan 471003, P. R. China
Jun-Ying Ma, School of Chemical Engineering and Pharmaceutics, Henan University of Science and Technology, Rovincial and Ministerial Co-construction of Collaborative Innovation Center for Non-ferrous Metal New Materials and Advanced Processing Technology, Luoyang, Henan 471003, P. R. China

Table 1: Data collection and handling.

Crystal:	Brown block
Size:	0.20 × 0.16 × 0.15 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.24 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	5547, 2725, 0.022
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2014
$N(param)_{refined}$:	169
Programs:	CrysAlis^{PRO} [1], Olex2 [2], SHELX [3]

Abstract
$C_{15}H_{14}O_2S$, monoclinic, $P2_1/c$ (no. 14), a = 13.5881(11) Å, b = 7.3129(9) Å, c = 13.3284(11) Å, β = 96.125(7)°, V = 1316.9(2) Å^3, Z = 4, $R_{gt}(F)$ = 0.0570, $wR_{ref}(F^2)$ = 0.1402, T = 293 K.

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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 (0.200 g, 2 mmol) and 2-naphthalenethiol (0.160 g, 1 mmol) in DMSO (1 mL) was added Cs_2CO_3 (0.326 mg, 1 mmol). The mixture was stirred at 45 °C under oxygen atmosphere for 10 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 (45:1) to give the desired (245 mg, 95%) as a white solid. Single crystals suitable for X-ray diffraction were obtained by crystallization of the title compound from ethyl acetate. Melting point: 88–89 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ 17.47 (s, 1H), 7.84–7.78 (m, 2H), 7.76(d, J = 8.6 Hz, 1H), 7.53–7.43 (m, 3H), 7.32 (d, J = 8.6 Hz, 1H), 2.43 (s, 6H). **^{13}C**

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

Atom	x	y	z	U_{iso}*/U_{eq}
S1	0.14502 (5)	0.74734 (11)	0.61439 (5)	0.0502 (2)
O1	0.12386 (15)	0.2882 (3)	0.45978 (18)	0.0690 (6)
H1	0.102 (3)	0.400 (8)	0.376 (4)	0.17 (2)*
O2	0.07901 (15)	0.5401 (4)	0.34290 (13)	0.0642 (6)
C1	0.33959 (17)	0.7432 (4)	0.56455 (16)	0.0389 (6)
H1A	0.3176	0.6754	0.5075	0.047*
C2	0.27362 (17)	0.7959 (4)	0.62994 (16)	0.0389 (6)
C3	0.30661 (18)	0.8987 (4)	0.71634 (16)	0.0448 (7)
H3	0.2616	0.9345	0.7605	0.054*
C4	0.40301 (19)	0.9461 (4)	0.73587 (17)	0.0474 (7)
H4	0.4232	1.0146	0.7931	0.057*
C5	0.57510 (19)	0.9388 (4)	0.6891 (2)	0.0548 (8)
H5	0.5976	1.0050	0.7466	0.066*
C6	0.6399 (2)	0.8874 (5)	0.6241 (2)	0.0631 (9)
H6	0.7065	0.9176	0.6376	0.076*
C7	0.6073 (2)	0.7887 (5)	0.5366 (2)	0.0622 (9)
H7	0.6524	0.7553	0.4920	0.075*
C8	0.51042 (19)	0.7414 (4)	0.51634 (19)	0.0491 (7)
H8	0.4897	0.6760	0.4581	0.059*
C9	0.44101 (17)	0.7910 (4)	0.58321 (16)	0.0387 (6)
C10	0.47349 (17)	0.8931 (4)	0.67077 (16)	0.0410 (6)
C11	0.12970 (16)	0.5916 (4)	0.51345 (17)	0.0415 (6)
C12	0.14117 (17)	0.4027 (5)	0.5316 (2)	0.0524 (7)
C13	0.1742 (2)	0.3276 (6)	0.6336 (3)	0.0793 (10)
H13A	0.1764	0.1965	0.6302	0.119*
H13B	0.1284	0.3640	0.6800	0.119*
H13C	0.2389	0.3738	0.6562	0.119*
C14	0.09843 (17)	0.6553 (4)	0.41561 (18)	0.0478 (7)
C15	0.0846 (2)	0.8509 (5)	0.3894 (2)	0.0712 (9)
H15A	0.0690	0.8630	0.3178	0.107*
H15B	0.1444	0.9166	0.4104	0.107*
H15C	0.0314	0.8998	0.4231	0.107*

NMR (101 MHz, $CDCl_3$) δ 198.4, 135.3, 133.9, 131.4, 128.9, 127.8, 126.8, 125.4, 123.6, 121.8, 101.4, 24.4.

Experimental details

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

Comment

β-dicarbonyl thioether belong to an important class of compounds, which are of great demand in organic synthesis as well as in the pharmaceutical industry [4, 5]. From a synthetic perspective, these compounds have frequently used as valuable starting materials or reactive intermediates in a variety of organic transformations [6–8]. For example, they have been used as precursors for a large number of target molecules [9]. Besides, β-dicarbonyl thioether have applications in the pharmaceutical and agrochemical industries. Examples of β-dicarbonyl thioethers as pharmaceutical building blocks or intermediates include anti-inflammatory [10], anti-HSV-1 [11], and antimicrobial properties [12]. In this paper we report the synthesis and crystal structure of a β-dicarbonyl thioether.

The assymmetric unit contains one molecule of the title compound, which is constructed by the acetylacetone and the 2-naphthalenethiol (see the figure). The acetylacetone fragment together with the sulfur almost in a strict plane, whereby the largest deviation for the S1 atom from the acetylacetone plane is 0.137 Å. The dihedral angle between the acetylacetone group and 2-naphthalenethiol group is found to be 88.26°. The C(2)–S(1)–C(11)–C(14) and C(2)–S(1)–C(11)–C(12) torsion angles are –97.72(19)° and 87.20(2)°. The C(2)–S(1)–C(11) bond angle is 104.71(11)°. The thioether bond distances are 1.758(3) Å for C(11)–S(1) and 1.773(2) Å for C(2)–S(1), respectively, which are typical C_{aryl}–S bond distances. The lengths of C(2)–C(1), C(2)–C(3) bond in benzene ring are 1.371(3) and 1.408(3) Å respectively. Within the acetylacetone unit, the dimensions and planarity are consistent with their adoption of a delocalized enol form. The bond lengths of C(11)–C(14), C(11)–C(12) are 1.407(3) Å and 1.409(4) Å respectively. In the crystal structure, the two oxygen atoms are linked by an intramolecular O(1)–H(1)···O(2) hydrogen bond. The distance of O(1)···H(1) is 1.400(5) Å and the distance of O(2)···H(1) is 1.140(6) Å. The structure of the molecule is similar to the stereo-configuration of the compound reported in the references [13–15]. The bond lengths and angles are all in the expected ranges. The complete set of X-ray diffraction data for the title compound was deposited to the Cambridge Crystallographic Data Centre (CCDC entry no. 2123340).

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

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

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