Le Dong, Ya-Fei Guo*, Jun-Ying Ma*, Jun-Ling Wang, Shu-Xiao Feng and Hui-Kang Huo

Crystal structure of (*E*)-3-((4-(*tert*-butyl)phenyl)thio)-4-hydroxypent-3-en-2-one, C₁₅H₂₀O₂S

Table 1: Data collection and handling.

Crystal:	Block, colourless
Size:	0.27 × 0.25 × 0.24 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.21 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω -scans
$\theta_{\max}$, completeness:	28.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	11,385, 3265, 0.033
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2549
$N(\text{param})_{\text{refined}}$:	181
Programs:	CrysAlis ^{PRO} [1], OLEX2 [2], SHELX [3]

The crystal structure is shown in the figure (for the disordered part only one component list shown). Tables 1 and 2 contain details on crystal structure and measurement conditions and a 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-*tert*-butylbenzenethiol (0.166 g, 1 mmol) in dimethyl sulfoxide (DMSO) (1 mL) was added Na₂CO₃ (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 Na₂SO₄ 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 (238 mg, 90%) as a white solid. Crystals were obtained by crystallization of the title compound from ethyl acetate. Melting point: 104–106 °C. ¹H NMR (400 MHz, CDCl₃, 298 K) δ 17.26 (s, 1H), 7.31 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8.4 Hz, 2H), 2.35 (s, 6H), 1.30 (s, 9H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 198.3, 148.4, 134.2, 126.2, 124.6, 102.0, 34.4, 31.4, 24.5.

Experimental details

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

<https://doi.org/10.1515/ncrs-2021-0365>

Received September 19, 2021; accepted October 29, 2021; published online November 18, 2021

Abstract

C₁₅H₂₀O₂S, monoclinic, $P2_1/c$ (No. 14), a = 12.8520(8) Å, b = 10.5864(8) Å, c = 11.2202(7) Å, β = 104.375(7)°, V = 1478.78(18) Å³, Z = 4, $R_{\text{gt}}(F)$ = 0.0655, $wR_{\text{ref}}(F^2)$ = 0.1781, T = 293 K.

CCDC no.: 2108461

*Corresponding authors: Ya-Fei Guo and Jun-Ying Ma, School of Chemical Engineering and Pharmaceuticals, Henan University of Science and Technology, Luoyang, Henan 471003, P. R. China, E-mail: guo.yafei@163.com (Y.-F. Guo), majy379@163.com (J.-Y. Ma). <https://orcid.org/0000-0001-9953-021X> (Y.-F. Guo) Le Dong, Jun-Ling Wang, Shu-Xiao Feng and Hui-Kang Huo, School of Chemical Engineering and Pharmaceuticals, Henan University of Science and Technology, Luoyang, Henan 471003, P. R. China. <https://orcid.org/0000-0002-9075-4089> (J.-L. Wang)

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
S1	0.63034 (5)	0.80321 (7)	0.49264 (6)	0.0609 (3)
O1	0.38156 (15)	0.8078 (2)	0.6385 (2)	0.0758 (6)
H1	0.4125	0.9026	0.6875	0.114 [*]
O2	0.50260 (16)	0.97776 (19)	0.73228 (18)	0.0731 (6)
C1	0.4173 (3)	0.6610 (3)	0.4957 (3)	0.0778 (8)
H1A	0.4651	0.5925	0.5277	0.117 [*]
H1B	0.4224	0.6808	0.4138	0.117 [*]
H1C	0.3449	0.6369	0.4939	0.117 [*]
C2	0.44780 (18)	0.7745 (2)	0.5763 (2)	0.0541 (6)
C3	0.54415 (17)	0.8414 (2)	0.5865 (2)	0.0462 (5)
C4	0.56855 (19)	0.9438 (2)	0.6692 (2)	0.0536 (6)
C5	0.6696 (2)	1.0182 (3)	0.6908 (3)	0.0818 (9)
H5A	0.6597	1.0980	0.7272	0.123 [*]
H5B	0.6878	1.0322	0.6139	0.123 [*]
H5C	0.7265	0.9724	0.7453	0.123 [*]
C6	0.71536 (16)	0.6827 (2)	0.57366 (19)	0.0416 (5)
C7	0.70896 (17)	0.6326 (2)	0.68557 (19)	0.0457 (5)
H7	0.6580	0.6631	0.7245	0.055 [*]
C8	0.77863 (17)	0.5368 (2)	0.73980 (19)	0.0452 (5)
H8	0.7739	0.5053	0.8156	0.054 [*]
C9	0.85475 (15)	0.4867 (2)	0.68514 (19)	0.0415 (5)
C10	0.85970 (18)	0.5392 (2)	0.5729 (2)	0.0519 (6)
H10	0.9104	0.5087	0.5337	0.062 [*]
C11	0.79198 (18)	0.6349 (2)	0.5182 (2)	0.0508 (6)
H11	0.7977	0.6677	0.4432	0.061 [*]
C12	0.92933 (19)	0.3783 (2)	0.7442 (2)	0.0554 (6)
C13 ^a	0.9882 (5)	0.4224 (6)	0.8811 (5)	0.0864 (13)
H13A ^a	0.9353	0.4431	0.9251	0.130 [*]
H13B ^a	1.0317	0.4953	0.8773	0.130 [*]
H13C ^a	1.0329	0.3551	0.9227	0.130 [*]
C14 ^a	1.0205 (5)	0.3530 (6)	0.6856 (6)	0.0844 (13)
H14A ^a	1.0590	0.4300	0.6820	0.127 [*]
H14B ^a	0.9925	0.3211	0.6038	0.127 [*]
H14C ^a	1.0681	0.2917	0.7335	0.127 [*]
C15 ^a	0.8667 (4)	0.2628 (5)	0.7556 (7)	0.0921 (19)
H15A ^a	0.9145	0.1981	0.7971	0.138 [*]
H15B ^a	0.8299	0.2336	0.6751	0.138 [*]
H15C ^a	0.8151	0.2820	0.8019	0.138 [*]
C15A ^b	0.8965 (6)	0.3143 (7)	0.8474 (9)	0.0921 (19)
H15D ^b	0.8241	0.2842	0.8192	0.138 [*]
H15E ^b	0.9008	0.3731	0.9136	0.138 [*]
H15F ^b	0.9436	0.2443	0.8758	0.138 [*]
C13A ^b	1.0427 (5)	0.4211 (8)	0.7740 (8)	0.0864 (13)
H13D ^b	1.0543	0.4817	0.8395	0.130 [*]
H13E ^b	1.0579	0.4592	0.7026	0.130 [*]
H13F ^b	1.0893	0.3499	0.7991	0.130 [*]
C14A ^b	0.9188 (6)	0.2733 (7)	0.6380 (7)	0.0844 (13)
H14D ^b	0.9707	0.2077	0.6660	0.127 [*]
H14E ^b	0.9316	0.3118	0.5655	0.127 [*]
H14F ^b	0.8479	0.2378	0.6192	0.127 [*]

^aOccupancy: 0.567(3), ^bOccupancy: 0.433(3).

Discussion

Acetylacetone derivatives are extensively employed in organic synthetic intermediates, analytical reagents, and other essential raw ingredients [4–6], which have been demonstrated to possess a wide range of biological and pharmaceutical activities such as sulfa-drugs [7], antipyretics [8], diabetes drugs [9], antiviral [10], pesticides [11], spectrofluorimetric method [12]. Besides, acetylacetone and its derivatives were frequently used as chelating ligands [13]. Examples for their coordination behavior were found for main group elements such as iron [14], aluminum [15], and palladium [16]. Up to date, a great number of acetylacetone derivatives have been reported. However, there are relatively few reports about a convenient and efficient protocol for the synthesis of α -sulfenylated carbonyl compounds based acetylacetone derivatives.

In this paper we report the synthesis and crystal structure of a novel sulfenylated carbonyl compound. The asymmetric unit contains one molecule of the title compound, which is constructed by the acetylacetone and the 4-*tert*-butylbenzenethiol moiety (see the Figure). The acetylacetone together with sulfur atom is almost in a strict plane, whereby the largest deviation for the S1 atom from the acetylacetone plane is 0.078 Å. The dihedral angle between the acetylacetone group and 4-*tert*-butylbenzenethiol were found to be 85°. The C(6)–S(1)–C(3)–C(2) and C(6)–S(1)–C(3)–C(4) torsion angles are –87.6(2)° and 95.2(2)°. The C(3)–S(1)–C(6) bond angle is 104.97(10)°. The thioether bond distances are 1.755(2) Å for C(3)–S(1) and 1.766(2) Å for C(6)–S(1), respectively, which are typical C–S bond distances. Within the acetylacetone unit, the dimensions and planarity are consistent with their adoption of a localized enol form. The bond lengths of C(3)–C(4), C(3)–C(2) are 1.410(3) and 1.407(3) Å respectively. The only intramolecular O(1)–H(1)···O(2) hydrogen bond is observed. The O(1)–H(1) and O(2)–H(1) bond lengths are 1.392 and 1.167 Å. The O(1)···O(2) separation is 2.440(3) Å. The structure of the molecule is similar to the stereo-configuration of the compound reported in the references. The bond lengths and angles are all in the expected ranges [17–19]. And no unusual intermolecular contacts, were observed in this crystal.

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

Research funding: This work was supported by the Programs for Science and Technology Development of Henan Province, China (No. 212102210650) and the Key Research Project for Colleges and Universities of Henan Province, China (No. 21B530002).

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

References

1. Oxford Diffraction, CrysAlis^{PRO} (version 1.171.33.42); Oxford Diffraction Ltd.: Oxford, UK, 2009.
2. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, 42, 339–341.
3. Sheldrick G. M. A short history of SHELX. *Acta Crystallogr.* 2008, A64, 112–122.
4. Al-Adiwish W. M., Tahir M. I., Siti-Noor-Adnalizawati A., Hashi S. F., Ibrahim N., Yaacob W. A. Synthesis, antibacterial activity and cytotoxicity of new fused pyrazolo[1,5-*a*]pyrimidine and pyrazolo[5,1-*c*][1,2,4]triazine derivatives from new 5-aminopyrazoles. *Eur. J. Med. Chem.* 2013, 64, 464–476.
5. Svistunova I. V., Sharutin V. V., Tretyakova G. O., Puzyrkov Z. N. Synthesis and structure of boron difluoride binuclear β -diketonates. *Inorg. Chim. Acta.* 2020, 501, 119230–119236.
6. Gupta V. K., Goyal R. N., Bachheti N., Singh L. P., Agarwal S. A copper-selective electrode based on bis(acetylacetonate) propylenediimine. *Talanta* 2005, 68, 193–197.
7. Darwish E., Fattah A., Attaby F., Al-Shayea O. Synthesis and antimicrobial evaluation of some novel thiazole, pyridone, pyrazole, chromene, hydrazone derivatives bearing a biologically active sulfonamide moiety. *Int. J. Mol. Sci.* 2014, 15, 1237–1254.
8. Glukhachev V. S., Il'yasov S. G., Kazantsev I. V., Shestakova E. O., Il'yasov D. S., El'tsov I. V., Nefedov A. A., Gatilov Y. V. New reaction products of acetylacetonate with semicarbazide derivatives. *ACS Omega* 2021, 6, 8637–8645.
9. Sanna D., Ugone V., Serra M., Garribba E. Speciation of potential anti-diabetic vanadium complexes in real serum samples. *J. Inorg. Biochem.* 2017, 173, 52–65.
10. Krohn K., Vukics K. First chemical synthesis of the antiviral agents $S_{25}O_2$ and $S_{25}O_7$. *Synthesis* 2007, 2007, 2894–2900.
11. Abunada N. M., Hassaneen H. M., Kandile N. G., Miqdad O. A. Synthesis and antimicrobial activity of some new pyrazole, fused pyrazolo[3,4-*d*]pyrimidine and pyrazolo[4,3-*e*][1,2,4]triazolo [1,5-*c*]pyrimidine derivatives. *Med. Sci.* 2008, 13, 1501–1517.
12. Omar M. A., Derayea S. M., Mostafa I. M. Development and validation of a stability-indicating spectrofluorimetric method for the determination of H1N1 antiviral drug (oseltamivir phosphate) in human plasma through the Hantzsch reaction. *RSC Adv.* 2015, 5, 27735–27742.
13. Kremer M., Englert U. *N* Donor substituted acetylacetonates – versatile ditopic ligands. *Z. Kristallogr. - Cryst. Mater.* 2018, 233, 437–452.
14. Hu X., Mao J., Sun Y., Chen H., Li H. Acetylacetonate-Fe catalyst modified by imidazol ionic compound and its application in aerobic oxidation of β -isophorone. *Catal. Commun.* 2009, 10, 1908–1912.
15. Pang X., Chen X., Du H., Wang X., Jing X. Enolic Schiff-base aluminum complexes and their application in lactide polymerization. *J. Organomet. Chem.* 2007, 692, 5605–5613.
16. Khranenko S. P., Bykova E. A., Gromilov S. A., Gallyamov M. R., Kozlova S. G., Moroz N. K., Korenev S. V. Novel mixed-ligand palladium complexes $[Pd_2(acac)_3NO_3]$ and $[Pd(acac)NO_3]_n$ involving O,O- and γ -C-bonded acetylacetonate linkers. *Polyhedron* 2012, 31, 272–277.
17. Olivier J. H., Haefele A., Retailleau P., Ziessel R. Borondipyromethene dyes with pentane-2,4-dione anchors. *Org. Lett.* 2010, 12, 408–411.
18. Jing N., Jian-Hua W., Zhong-Hai N. Synthesis, crystal structure and optical property of 1,6-bis(*p*-tolylthio)pyrene, $C_{30}H_{22}S_2$. *Z. Kristallogr. N. Cryst. Struct.* 2021, 236, 21–23.
19. Rashid M. A., Rasool N., Adeel M., Reinke H., Fischer C., Langer P. Synthesis of functionalized diaryl sulfides based on regioselective one-pot cyclizations of 1,3-bis(trimethylsilyloxy)-1,3-butadienes. *Tetrahedron* 2008, 64, 3782–3793.