

Xiaofan Bai, Ziwen Zhang, Wei Guo, Yongkang Zhang, Liqiang Zhang, Huihui Liu, Haixia Wu* and Yong Li*

The crystal structure of 2,6-di-*tert*-butyl-4-(4-(methylthio)benzylidene)cyclohexa-2,5-dien-1-one, C₂₂H₂₈OS

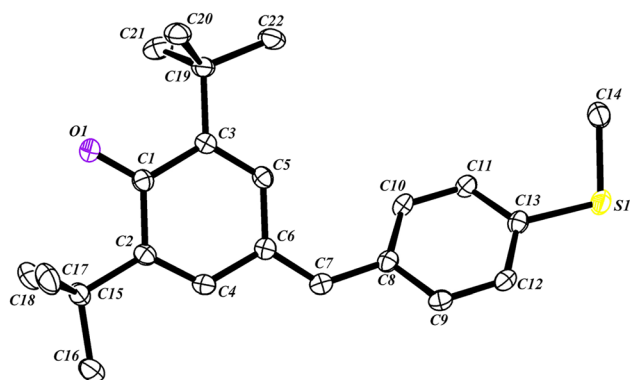


Table 1: Data collection and handling.

Crystal:	Block, colorless
Size:	0.12 × 0.11 × 0.11 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.17 mm ⁻¹
Diffractometer, scan mode:	ROD, Synergy Custom DW system, ϕ and ω -scans
$\theta_{\max}$, completeness:	29.3°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	14307, 4301, 0.030
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3558
$N(\text{param})_{\text{refined}}$:	224
Programs:	CrysAlis ^{PRO} [1], OLEX-II [2], SHELX [3, 4]

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Abstract

C₂₂H₂₈OS, monoclinic, P2₁/n (no. 14), $a = 6.7729(3)$ Å, $b = 17.3973(6)$ Å, $c = 16.6277(6)$ Å, $\beta = 92.380(3)^\circ$, $V = 1957.55(13)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.041$, $wR_{\text{ref}}(F^2) = 0.100$, $T = 90$ 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.

***Corresponding authors:** Haixia Wu, College of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, #26 Yuxiang Street, Yuhua District, Shijiazhuang, 050018, China, E-mail: wuhaixia@hebut.edu.cn; and Yong Li, College of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, #26 Yuxiang Street, Yuhua District, Shijiazhuang, 050018, China; and Shijiazhuang No. 4 Pharmaceutical Co. Ltd, Quality & Technology Center, No. 288, Zhujiang Road, Hi-Tech industrial and Development Zone, Shijiazhuang, 050000, China, E-mail: ly318418@163.com
Xiaofan Bai, Ziwen Zhang, Wei Guo, Yongkang Zhang, Liqiang Zhang and Huihui Liu, College of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, #26 Yuxiang Street, Yuhua District, Shijiazhuang, 050018, China. <https://orcid.org/0000-0003-1699-0021> (X. Bai). <https://orcid.org/0000-0003-1189-5682> (W. Guo)

Source of material

All chemicals and solvents are analytical grade. The starting materials 2,6-di-*tert*-butylphenol (0.1 mmol, 1.0 eq) and 4-methylsulfanyl-benzaldehyde (0.13 mmol, 1.3 eq) were mixed, dissolved in toluene (0.25 M), and then placed in a Dean–Stark device for sonication for 15 min. The reaction was heated at 393 K. Piperidine (2 eq) was added dropwise to the reaction at a constant speed within 3 h. After the reaction was completed, the temperature was adjusted to 383 K, and an appropriate amount of acetic acid anhydride was added. After 15 min, the reaction solution was poured into ice water. Extract with dichloromethane (25 mL × 3). The organic phases were combined, dried over anhydrous Na₂SO₄, the organic phase was concentrated under reduced pressure, and the residue was purified by column chromatography using petroleum ether as eluent to obtain the product with a yield of 91.3%. The product was dissolved with an appropriate amount of methanol at room temperature, and the title compound was obtained as crystals after slowly evaporating the solvent.

Experimental details

Using Olex2 [2], the structure was solved with the SHELXT [3] structure solution program and refined with the SHELXL [4] refinement package. All H atoms were positioned

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
S1	0.00756 (6)	0.65263 (2)	0.64058 (2)	0.02640 (12)
O1	1.15916 (17)	0.71746 (6)	0.23651 (7)	0.0277 (3)
C1	1.0309 (2)	0.68243 (8)	0.27213 (8)	0.0188 (3)
C2	0.9601 (2)	0.60623 (8)	0.24299 (8)	0.0184 (3)
C3	0.9387 (2)	0.71763 (8)	0.34295 (8)	0.0168 (3)
C4	0.8152 (2)	0.57147 (8)	0.28237 (8)	0.0199 (3)
H4	0.772509	0.522082	0.264554	0.024*
C5	0.7880 (2)	0.68036 (8)	0.37669 (8)	0.0181 (3)
H5	0.723464	0.704559	0.419556	0.022*
C6	0.7208 (2)	0.60531 (8)	0.35044 (8)	0.0185 (3)
C7	0.5714 (2)	0.56579 (8)	0.38399 (8)	0.0199 (3)
H7	0.543471	0.516896	0.360749	0.024*
C8	0.4476 (2)	0.58714 (8)	0.45024 (8)	0.0186 (3)
C9	0.2497 (2)	0.56358 (8)	0.44567 (9)	0.0200 (3)
H9	0.204160	0.532010	0.402126	0.024*
C10	0.5122 (2)	0.62896 (8)	0.51841 (8)	0.0196 (3)
H10	0.647227	0.643473	0.524366	0.023*
C11	0.3836 (2)	0.64959 (8)	0.57724 (8)	0.0198 (3)
H11	0.430954	0.677793	0.623002	0.024*
C12	0.1193 (2)	0.58535 (8)	0.50327 (9)	0.0199 (3)
H12	−0.015438	0.570418	0.497649	0.024*
C13	0.1839 (2)	0.62901 (8)	0.56949 (9)	0.0196 (3)
C14	0.0916 (2)	0.74458 (9)	0.67660 (10)	0.0288 (4)
H14A	0.101660	0.779940	0.631077	0.043*
H14B	0.221603	0.738947	0.704103	0.043*
H14C	−0.002480	0.765121	0.714324	0.043*
C15	1.0521 (2)	0.57099 (8)	0.16859 (9)	0.0222 (3)
C16	0.9608 (3)	0.49260 (9)	0.14774 (10)	0.0314 (4)
H16A	0.983176	0.457429	0.193242	0.047*
H16B	1.022333	0.471621	0.100157	0.047*
H16C	0.818445	0.498591	0.136477	0.047*
C17	1.0151 (3)	0.62373 (9)	0.09509 (9)	0.0314 (4)
H17A	0.872583	0.630748	0.085230	0.047*
H17B	1.071769	0.600240	0.047698	0.047*
H17C	1.077455	0.673771	0.105578	0.047*
C18	1.2742 (3)	0.55909 (10)	0.18434 (11)	0.0319 (4)
H18A	1.336514	0.608385	0.198411	0.048*
H18B	1.332147	0.538474	0.135811	0.048*
H18C	1.296039	0.522789	0.228890	0.048*
C19	1.0153 (2)	0.79546 (8)	0.37396 (8)	0.0207 (3)
C20	0.9893 (3)	0.85790 (8)	0.30874 (9)	0.0249 (3)
H20A	1.070696	0.845183	0.263214	0.037*
H20B	1.030594	0.907734	0.331191	0.037*
H20C	0.850160	0.860531	0.290301	0.037*
C21	1.2348 (3)	0.78843 (9)	0.40011 (10)	0.0291 (4)
H21A	1.250867	0.748615	0.441559	0.044*
H21B	1.282185	0.837730	0.421912	0.044*
H21C	1.311282	0.774464	0.353547	0.044*
C22	0.9018 (3)	0.82178 (9)	0.44694 (10)	0.0319 (4)
H22A	0.762170	0.829009	0.430952	0.048*
H22B	0.957146	0.870448	0.467216	0.048*
H22C	0.913665	0.782704	0.489323	0.048*

geometrically and treated as riding, and U_{iso} was fixed at 1.2 times of C(H) groups and at 1.5 times of C(H, H, H) groups.

Discussion

The *p*-quinone methides is a unique class of compounds with two α , β -unsaturated carbonyl groups [5]. It is a widely used intermediate in many chemical, pharmaceutical and biosynthesis [6, 7]. The structure of cyclohexenone and exocyclic conjugated double bonds endows it with aromatization and electron-deficient driving forces [8, 9], thus exhibiting unique electrophilic reactivity and prone to 1,6-addition reactions, and has good research value. Such compounds [10] can be extracted from natural products by biological and chemical methods, or they can be directly synthesized by chemical methods [11, 12]. The presence of the electrophilic methylthio group in the title compound makes it more susceptible to 1,6-addition reaction, thereby enhancing the activity of this class of compounds. Many similar crystal structures have been reported [13–16]. The structures of the compounds were identified by NMR and X-ray diffraction.

The unit contains one molecule, as shown in the figure, two tert-butyl groups replace the two hydrogen atoms at the C2 and C3 positions, respectively, and the electrophilic methylthio group replaces the hydrogen atom at the C13 position. The bond lengths and bond angles of this structure are within reasonable ranges [17]. The cyclohexadiene plane (C1–C2–C4–C6–C5–C3) and the benzene ring plane (C8–C9–C12–C13–C11–C10) make an angle of 37.46°. The bond lengths of O1–C1, C14–S1, C13–S1 are 1.233(18), 1.793(16), 1.763(15) Å, respectively. The torsion angles of C6–C7–C8–C9, C6–C7–C8–C10, C14–S1–C13–C11 are 144.56(15)°, −35.95(2)°, and 33.94(14)°. The angle of C14–S1–C13 is 102.56(7)°. The distance from O1 to the plane of the benzene ring (C8–C9–C12–C13–C11–C10) is 2.763 Å, and the distance of S1 to the cyclohexadiene plane (C1–C2–C4–C6–C5–C3) is 0.561 Å.

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