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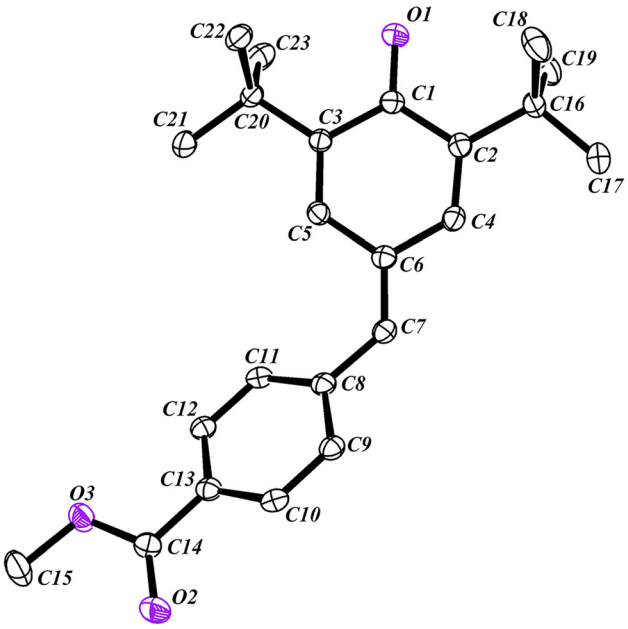
The crystal structure of methyl 4-((3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl) benzoate, $C_{23}H_{28}O_3$



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Abstract

$C_{23}H_{28}O_3$, monoclinic, $P2_1/n$ (no. 14), a = 7.3985 (2) Å, b = 16.6978 (5) Å, c = 16.5137 (5) Å, β = 96.699(3)°, V = 2026.15 (10) Å^3, Z = 4, $R_{gt}(F)$ = 0.0428, $wR_{ref}(F^2)$ = 0.1116, 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.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.13 × 0.12 × 0.11 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	0.08 mm^{-1}
Diffractometer, scan mode:	ROD, Synergy Custom DW, ω
θ_{max}, completeness:	29.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	14,806, 4550, 0.025
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 3557
$N(param)_{refined}$:	242
Programs:	CrysAlis^{PRO} [1], Olex2 [2], SHELX [3, 4]

Source of material

All chemicals and solvents are of analytical grade. 2,6-di-*tert*-butylphenol (5 g, 1 eq) and methyl 4-formylbenzoate (4.8 g, 1.2 eq) were mixed, placed in a three-necked flask, and 30 mL of toluene solution was added. The reaction was carried out at 418.15 K for 14 h. During this period, piperidine (4.127 g, 2 eq) was added dropwise to the system at a uniform speed, and the dripping was completed within 3 h. After the reaction of the phenol is completed, the temperature is adjusted to 373.15 K, an appropriate amount of acid anhydride is added, and stirring is continued for 15–30 min. The reaction mixture was taken out and poured into ice water, extracted with ethyl acetate (25 mL × 3), the organic phases were combined, anhydrous Na_2SO_4 was added to remove water. The organic phase was concentrated in vacuo, and the residue was purified by column chromatography to obtain colorless lumpy solid with a yield of 86.5%. Crystals were grown in methanol at room temperature.

Experimental details

Using Olex2 [2], the structure was solved with the SHELXT [3] structure solution program using Intrinsic Phasing and

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2). Since all hydrogen atoms in this structure are not conformational isomers, * is used to distinguish all hydrogen atoms.

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O1	1.13642 (14)	0.27390 (6)	0.23800 (6)	0.0335 (3)
O2	−0.03733 (13)	0.39303 (6)	0.60168 (6)	0.0339 (3)
O3	0.15363 (12)	0.29399 (6)	0.64533 (6)	0.0271 (2)
C1	1.01974 (17)	0.31106 (7)	0.26996 (8)	0.0200 (3)
C2	0.95457 (17)	0.39032 (7)	0.23743 (7)	0.0187 (3)
C3	0.93805 (17)	0.27636 (7)	0.34051 (7)	0.0180 (3)
C4	0.82478 (17)	0.42798 (7)	0.27365 (8)	0.0201 (3)
H4	0.785845	0.479249	0.253675	0.024*
C5	0.80500 (17)	0.31712 (7)	0.37159 (8)	0.0191 (3)
H5	0.750552	0.293907	0.415339	0.023*
C6	0.74090 (17)	0.39505 (7)	0.34122 (8)	0.0187 (3)
C7	0.60229 (17)	0.43664 (7)	0.36893 (8)	0.0195 (3)
H7	0.576314	0.486720	0.342844	0.023*
C8	0.48672 (17)	0.41698 (7)	0.43220 (8)	0.0190 (3)
C9	0.30617 (17)	0.44434 (7)	0.42073 (8)	0.0199 (3)
H9	0.266372	0.476174	0.374376	0.024*
C10	0.18548 (17)	0.42578 (7)	0.47564 (8)	0.0203 (3)
H10	0.063536	0.444515	0.466720	0.024*
C11	0.54466 (17)	0.37432 (7)	0.50378 (8)	0.0194 (3)
H11	0.668393	0.358404	0.514656	0.023*
C12	0.42359 (17)	0.35515 (7)	0.55871 (8)	0.0192 (3)
H12	0.463983	0.325317	0.606388	0.023*
C13	0.24241 (17)	0.37958 (7)	0.54415 (8)	0.0191 (3)
C14	0.10514 (17)	0.35846 (7)	0.59937 (8)	0.0210 (3)
C15	0.0191 (2)	0.26714 (10)	0.69586 (10)	0.0354 (4)
H15A	−0.097228	0.258774	0.661988	0.053*
H15B	0.003882	0.307703	0.737412	0.053*
H15C	0.059181	0.216694	0.722482	0.053*
C16	1.03457 (18)	0.42445 (7)	0.16303 (8)	0.0224 (3)
C17	0.9459 (2)	0.50445 (9)	0.13668 (10)	0.0394 (4)
H17A	0.814598	0.496792	0.122774	0.059*
H17B	0.998607	0.524764	0.088944	0.059*
H17C	0.967573	0.543083	0.181437	0.059*
C18	0.9991 (2)	0.36622 (9)	0.09098 (9)	0.0341 (4)
H18A	1.068747	0.316899	0.103289	0.051*
H18B	1.036931	0.391065	0.041900	0.051*
H18C	0.869016	0.353510	0.081775	0.051*
C19	1.2395 (2)	0.43913 (9)	0.18265 (9)	0.0320 (3)
H19A	1.260405	0.480810	0.224470	0.048*
H19B	1.289772	0.456493	0.133182	0.048*
H19C	1.299392	0.389472	0.202826	0.048*
C20	1.00482 (19)	0.19414 (7)	0.37285 (8)	0.0221 (3)
C21	0.9084 (2)	0.16911 (8)	0.44624 (9)	0.0336 (4)
H21A	0.931159	0.209270	0.489507	0.050*
H21B	0.955243	0.117076	0.466551	0.050*
H21C	0.777205	0.165002	0.429547	0.050*
C22	0.9629 (2)	0.13028 (7)	0.30615 (8)	0.0263 (3)
H22A	0.832721	0.131366	0.286431	0.040*
H22B	0.995674	0.077264	0.328731	0.040*
H22C	1.033493	0.141515	0.260797	0.040*
C23	1.2105 (2)	0.19646 (8)	0.40010 (9)	0.0320 (3)
H23A	1.275230	0.209686	0.353358	0.048*
H23B	1.250798	0.143961	0.421771	0.048*
H23C	1.236644	0.237197	0.442571	0.048*

refined with the SHELXL [4] refinement package using Least Squares minimisation. All H atoms were positioned geometrically and treated as riding, and U_{iso} was fixed at 1.2 times of C(H) groups and at 1.5 times of methyl groups.

Comment

P-Quinone Mehtides (p-QMs) are a class of cyclohexadiene compounds reported at the beginning of the last century [5]. Its structural unit is an important part of many cationic dyes and acid-base indicators [6–8], and is widely found in natural products and active drug molecules. In the process of chemistry, biology and materials science research [9], p-methylene quinone has attracted much attention as a key intermediate. P-QMs are electron-deficient alkenes generated by replacing one carbonyl group of benzoquinone with a carbon-carbon double bond [10, 11]. The title compound is a p-QM with a special dienone structure that is highly electrophilic and thus easily polarized into an ionic form. The presence of the electrophilic ester group and the two tert-butyl groups around the carbonyl can make it more stable [12]. Similar crystal structures have been reported [13–15].

The asymmetric unit of the title structure consists of a methyl 4-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)benzoate molecule. In the title compound, two tert-butyl groups replace the two hydrogen atoms at the C2 and C3 positions of the cyclohexadiene, respectively, and the electrophilic ester group replaces the hydrogen atom at the benzene ring position, as shown in the figure. The bond lengths and bond angles are within the appropriate range [11]. For example, the dihedral angle between the cyclohexadiene plane (C1–C2–C4–C6–C5–C3) and the benzene ring plane (C8–C9–C10–C13–C12–C11) is 33.49°. The torsion angles of C15–O3–C14–O2, C6–C7–C8–C9 and C6–C7–C8–C11 are 2.16 (19)°, −146.93 (13)°, and 34.38 (2)°, respectively. The angles of C15–O3–C14, C13–C14–O3, C13–C14–O2 are 114.80 (10)°, 112.41 (11)°, 124.66 (12)°, respectively. The bond lengths of O1–C1, O2–C14, O3–C15, O3–C14 are 1.231 (15), 1.206 (16), 1.443 (16), 1.342 (15). The distance (the minimum length) from O1 to the plane of the benzene ring (C8–C9–C10–C13–C12–C11) is 2.704.

Author contributions: Pengda Zhai: Writing – Original Draft; Hui Guan: Methodology; Junna Wang: Formal analysis; Yongkang Zhang: Data Curation; Haixia Wu: Writing - Review & Editing; Yifan Jia and Siye Li: Visualization; Juchuan Shan: Supervision; Yue Ding: Project administration. All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

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