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Crystal structure of 2,6-di-tert-butyl-4-(4-methoxybenzylidene)cyclohexa-2,5-dien-1-one, C₂₂H₂₈O₂

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.12 × 0.1 × 0.08 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.07 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω -scans
$\theta_{\max}$, completeness:	29.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	8174, 3760, 0.035
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2949
$N(\text{param})_{\text{refined}}$:	224
Programs:	CRYSA LIS ^{PRO} [1], SHELX [2], OLEX2 [3], DIAMOND [4]

<https://doi.org/10.1515/ncrs-2021-0394>

Received October 12, 2021; accepted November 5, 2021;

published online November 22, 2021

Abstract

C₂₂H₂₈O₂, orthorhombic, *Pna*2₁ (No. 33), $a = 12.0841(9)$ Å, $b = 16.6946(12)$ Å, $c = 9.3837(8)$ Å, $\beta = 90^\circ$, $V = 1893.1(3)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0497$, $wR_{\text{ref}}(F^2) = 0.1057$, $T = 220$ K.

CCDC no.: 2114824

The crystal 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.

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Source of material

All chemicals, and solvents are of analytical grade and are commercially available. In a Dean-Stark apparatus, a solution of 2,6-di-tert-butylphenol (0.1 mmol; 1.0 eq) and 4-methoxy benzaldehyde (0.1 mmol; 1.0 eq) in toluene (0.25 M) was heated at 145 °C. Piperidine (2 eq) was added within 3 h and heating under reflux was continued for 14 h. Acetic anhydride was added and stirring was continued for 15 min. The reaction mixture was poured on ice-water and extracted with ethyl acetate (25 mL × 3). The combined organic phases were dried over Mg₂SO₄, and the solvent was removed under reduced pressure. The organic phase was evaporated to dryness, and the residue was purified by column chromatography to obtain the desired product as a yellow solid with a yield of 90.3%. ¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, $J = 2.5$ Hz, 1H), 7.47 – 7.42 (m, 2H), 7.13 (s, 1H), 7.02 – 6.95 (m, 3H), 3.88 (s, 3H), 1.32 (d, $J = 7.9$ Hz, 18H). Crystals were grown in methanol at room temperature.

Experimental details

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

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}
O2	0.76425 (14)	0.44539 (9)	0.38948 (18)	0.0475 (4)
O1	0.21883 (13)	0.81449 (10)	0.84953 (18)	0.0481 (4)
C9	0.62481 (16)	0.66207 (12)	0.4710 (2)	0.0312 (5)
C17	0.76142 (16)	0.58373 (13)	0.3363 (2)	0.0307 (5)
C11	0.65543 (16)	0.52348 (12)	0.5462 (2)	0.0289 (5)
C16	0.72901 (17)	0.51250 (13)	0.4212 (2)	0.0319 (5)
C22	0.70948 (17)	0.65346 (13)	0.3635 (2)	0.0337 (5)
C5	0.47242 (18)	0.75093 (12)	0.5711 (2)	0.0356 (5)
C10	0.60748 (16)	0.59511 (12)	0.5654 (2)	0.0309 (5)
C18	0.84886 (18)	0.57461 (13)	0.2189 (2)	0.0366 (5)
C2	0.2988 (2)	0.79013 (13)	0.7560 (3)	0.0379 (5)
C12	0.63383 (17)	0.45253 (12)	0.6465 (2)	0.0329 (5)
C3	0.30653 (18)	0.71352 (13)	0.7012 (2)	0.0381 (5)
C7	0.3746 (2)	0.84817 (13)	0.7160 (3)	0.0424 (6)
C4	0.39264 (17)	0.69507 (13)	0.6091 (2)	0.0374 (5)
C6	0.45920 (19)	0.82901 (13)	0.6239 (3)	0.0415 (6)
C8	0.56737 (17)	0.73216 (13)	0.4806 (3)	0.0370 (5)
C13	0.5648 (2)	0.47827 (15)	0.7746 (3)	0.0491 (7)
C20	0.95435 (19)	0.53590 (15)	0.2783 (3)	0.0509 (7)
C14	0.57030 (19)	0.38670 (13)	0.5662 (3)	0.0470 (6)
C21	0.8817 (2)	0.65613 (15)	0.1572 (3)	0.0519 (7)
C15	0.74335 (19)	0.41809 (14)	0.7052 (3)	0.0451 (6)
C19	0.8022 (2)	0.52323 (16)	0.0972 (3)	0.0518 (7)
C1	0.1457 (2)	0.75519 (15)	0.9049 (3)	0.0542 (7)
H10	0.56081 (16)	0.60190 (12)	0.6433 (2)	0.0371 (6)*
H22	0.72913 (17)	0.69829 (13)	0.3104 (2)	0.0404 (6)*
H4	0.39704 (17)	0.64360 (13)	0.5716 (2)	0.0449 (7)*
H3	0.25464 (18)	0.67477 (13)	0.7258 (2)	0.0458 (7)*
H7	0.3683 (2)	0.90001 (13)	0.7513 (3)	0.0509 (7)*
H6	0.50871 (19)	0.86868 (13)	0.5961 (3)	0.0498 (7)*
H8	0.59179 (17)	0.77340 (13)	0.4219 (3)	0.0444 (6)*
H13a	0.6022 (7)	0.5206 (7)	0.8244 (10)	0.0737 (10)*
H13b	0.4939 (6)	0.4970 (9)	0.7426 (3)	0.0737 (10)*
H13c	0.5548 (12)	0.4335 (3)	0.8374 (9)	0.0737 (10)*
H20a	0.9842 (8)	0.5690 (5)	0.3526 (13)	0.0763 (10)*
H20b	0.9370 (3)	0.4840 (5)	0.3161 (17)	0.0763 (10)*
H20c	1.0079 (6)	0.5305 (9)	0.2033 (5)	0.0763 (10)*
H14a	0.5006 (7)	0.4075 (3)	0.5339 (16)	0.0705 (9)*
H14b	0.6130 (7)	0.3693 (7)	0.4857 (11)	0.0705 (9)*
H14c	0.5576 (12)	0.3422 (4)	0.6288 (6)	0.0705 (9)*
H21a	0.8183 (4)	0.6807 (5)	0.1138 (16)	0.0778 (10)*
H21b	0.9089 (13)	0.6899 (4)	0.2323 (4)	0.0778 (10)*
H21c	0.9385 (10)	0.64889 (18)	0.0869 (13)	0.0778 (10)*
H15a	0.7884 (6)	0.3997 (9)	0.6276 (3)	0.0676 (9)*
H15b	0.7822 (7)	0.4591 (3)	0.7567 (15)	0.0676 (9)*
H15c	0.7276 (2)	0.3741 (7)	0.7680 (14)	0.0676 (9)*
H19a	0.7842 (13)	0.4709 (4)	0.1327 (5)	0.0777 (10)*
H19b	0.7367 (8)	0.5481 (5)	0.0598 (12)	0.0777 (10)*
H19c	0.8565 (6)	0.5186 (9)	0.0230 (8)	0.0777 (10)*
H1a	0.0981 (10)	0.7364 (8)	0.8302 (5)	0.0813 (11)*
H1b	0.1880 (2)	0.7112 (5)	0.9419 (17)	0.0813 (11)*
H1c	0.1018 (11)	0.7781 (3)	0.9798 (13)	0.0813 (11)*

Discussion

P-Methylenebenzaldehyde is an important derivative with a unique structure in organic chemistry change to *P*-Methylene benzoquinone is an important derivative with a unique structure in organic chemistry [5]. Since it is easily polarized into an ionic form [6], it is very active [7]. It is generally believed that there is an electron-withdrawing group or aromatic ring compound on the seventh carbon outside the ring [8], and there are very large substituents around the group that stabilize the *p*-methylene benzaldehyde [9]. This kind of compound was first reported in 1903 [10]. Functionalized *p*-QMs units are found in many natural products, *p*-QMs are also active intermediates in many chemicals, drugs, and biological reactions [11–13]. Many similar crystal structures have been reported [14–17]. The structure of the title compound was elucidated by spectroscopic methods (NMR) and X-ray diffraction.

The title compound is a non-planar molecule (see the figure) with all bond lengths and angles in the crystal structure within the normal range [14–17]. In addition, the dihedral angle between the benzene ring plane (C9–C10–C11–C16–C17–C22) and the cyclohexadiene plane (C2–C3–C4–C5–C6–C7) is 33.3° (77). The bond lengths of C12–C13, C12–C14, C12–C15C and C18–C19, C18–C20, C18–C21, respectively, are 1.525(3), 1.538(3), 1.545(3) and 1.536(3), 1.534(3), 1.531(3) Å.

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 Natural Science Foundation of Hebei Province (B2016208054) and Supported by the Doctoral Research Foundation of Shijiazhuang University (20BS014).

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

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