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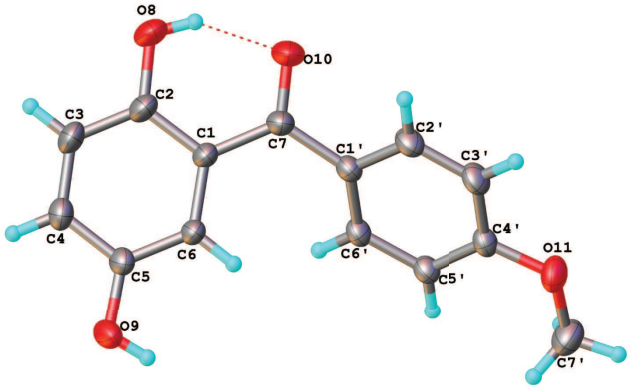
Crystal structure of (2,5-dihydroxyphenyl)-(4-methoxyphenyl)methanone, $C_{14}H_{12}O_4$



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Abstract

$C_{14}H_{12}O_4$, orthorhombic, $Pca2_1$ (no. 29), $a = 22.6015(12)$ Å, $b = 7.1344(4)$ Å, $c = 7.3789(4)$ Å, $V = 1189.83(11)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.065$, $wR_{ref}(F^2) = 0.186$, $T = 298$ K.

CCDC no.: 1442723

The crystal structure is shown in the figure, Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

A 100 mL benzene solution of the 1,4-benzoquinone (1 mmol) and 4-methoxybenzaldehyde (7.5 mmol), was placed into the outer jacket of a Liebig condenser. The solution was bubbled with nitrogen (2 min), the flask was sealed with a septum and then irradiated for six days (total illumination time of 30 h), under solar radiation conditions in the range 800–1100 Watts/m^2 (November–March). The solvent was evaporated under reduced pressure and the residue was chromatographed on silica gel (3:1 petroleum ether/ethyl acetate) obtaining yellow crystals with 79% of yield. Analysis: Solid crystalline **m.p.** 144–145 °C. **IR** (KBr) ν (cm^{-1}): 3343 (O—H), 1631 (C=O). **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 3.87 (s, 3H, OMe), 6.90 (d, 1H, $J = 8.8$ Hz, 3-H or 4-H), 6.97 (d, 2H, J=8.8 Hz, 2′-H + 3′-H or 5′-H + 6′-H), 7.08 (m, 2H, 4-H or 3-H + 6-H), 7.72 (d, 2H, $J = 8.8$ Hz, 6′-H + 5′-H or 3′-H + 2′-H), 8.32 (s, 1H, 5-OH), 11.38 (s, 1H, 2-OH); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 55.5, 113.6, 115.9, 118.1, 118.7, 119.2, 122.4, 124.4, 130.4, 131.8, 148.7, 155.9, 162.8, 199.7; HRMS (APCI): $[M+H]^+$ calcd for $C_{14}H_{12}O_4$: 244.07356; found: 244.07360.

Table 1: Data collection and handling.

Crystal:	Yellow, block, size 0.25×0.30×0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.00 cm^{-1}
Diffractometer, scan mode:	Bruker AXS D8-Venture, Triumph-IμS-Cu, φ
$2\theta_{max}$:	80.57°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	39770, 7393
$N(param)_{refined}$:	166
Programs:	SHELXL [1], OLEX2 [2]

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

Atom	Site	x	y	z	U_{iso}
H(9)	4a	−0.7900	−0.8724	−0.4803	0.083
H(8)	4a	−0.6984	−0.0679	−0.5395	0.099
H(6')	4a	−0.6367	−0.6927	−0.6763	0.034
H(5')	4a	−0.5581	−0.9021	−0.6775	0.035
H(6)	4a	−0.7076	−0.6821	−0.4700	0.036
H(2')	4a	−0.5494	−0.3644	−0.3240	0.042
H(3')	4a	−0.4727	−0.5755	−0.3172	0.042
H(3)	4a	−0.8398	−0.1921	−0.5543	0.054
H(7'A)	4a	−0.4599	−0.9999	−0.7232	0.075
H(7'B)	4a	−0.4908	−1.1150	−0.5689	0.075
H(7'C)	4a	−0.4215	−1.1030	−0.5769	0.075
H(4)	4a	−0.8740	−0.4956	−0.5285	0.047

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Table 3: Atomic displacement parameters (Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(11)	4*a*	−0.45915(6)	−0.8726(2)	−0.4869(3)	0.0269(5)	0.0457(7)	0.0553(9)	0.0077(5)	−0.0074(7)	−0.0069(8)
O(9)	4*a*	−0.81691(7)	−0.7953(2)	−0.4795(4)	0.0267(6)	0.0305(6)	0.108(2)	−0.0043(5)	0.0141(9)	−0.0087(9)
O(8)	4*a*	−0.73449(8)	−0.0729(2)	−0.5487(4)	0.0420(8)	0.0234(6)	0.133(3)	0.0061(5)	0.007(1)	0.0059(9)
O(10)	4*a*	−0.63125(8)	−0.1933(2)	−0.4939(5)	0.0375(7)	0.0244(6)	0.138(2)	−0.0057(5)	0.001(1)	−0.002(1)
C(6')	4*a*	−0.60369(7)	−0.6687(2)	−0.6049(3)	0.0212(5)	0.0302(6)	0.0347(7)	−0.0028(5)	−0.0031(5)	−0.0029(6)
C(5')	4*a*	−0.55664(7)	−0.7950(2)	−0.6058(3)	0.0240(5)	0.0290(6)	0.0335(6)	−0.0029(5)	−0.0014(5)	−0.0045(6)
C(1')	4*a*	−0.60204(6)	−0.5073(2)	−0.4990(3)	0.0225(5)	0.0263(5)	0.0400(7)	−0.0035(4)	0.0012(6)	−0.0027(7)
C(6)	4*a*	−0.73381(6)	−0.5838(2)	−0.4902(3)	0.0222(5)	0.0217(5)	0.0471(8)	0.0020(4)	0.0027(6)	−0.0014(7)
C(2')	4*a*	−0.55160(8)	−0.4731(3)	−0.3933(3)	0.0281(7)	0.0330(7)	0.0441(9)	−0.0058(6)	−0.0018(7)	−0.0100(7)
C(5)	4*a*	−0.79390(7)	−0.6195(2)	−0.4991(3)	0.0230(5)	0.0273(6)	0.0488(9)	0.0008(4)	0.0039(7)	−0.0048(7)
C(2)	4*a*	−0.75257(9)	−0.2537(3)	−0.5320(4)	0.0325(7)	0.0241(6)	0.068(2)	0.0071(6)	0.0032(9)	0.0011(8)
C(4')	4*a*	−0.50726(6)	−0.7589(2)	−0.4977(3)	0.0206(5)	0.0322(6)	0.0338(7)	−0.0018(4)	−0.0020(6)	−0.0009(7)
C(1)	4*a*	−0.71184(7)	−0.4010(2)	−0.5113(3)	0.0237(5)	0.0205(5)	0.050(1)	0.0024(4)	0.0017(6)	−0.0017(7)
C(3')	4*a*	−0.50535(8)	−0.5982(3)	−0.3906(3)	0.0255(6)	0.0395(9)	0.0412(9)	−0.0048(6)	−0.0069(6)	−0.0075(7)
C(3)	4*a*	−0.81314(9)	−0.2902(3)	−0.5389(4)	0.0295(7)	0.0327(8)	0.072(2)	0.0107(6)	−0.0003(8)	0.0021(9)
C(7')	4*a*	−0.4577(1)	−1.0360(4)	−0.5980(5)	0.041(1)	0.042(1)	0.067(2)	0.0115(9)	−0.004(1)	−0.011(1)
C(4)	4*a*	−0.83357(8)	−0.4717(3)	−0.5231(4)	0.0238(6)	0.0366(8)	0.057(1)	0.0047(5)	0.0007(7)	−0.0024(8)
C(7)	4*a*	−0.64826(7)	−0.3600(2)	−0.5016(4)	0.0272(6)	0.0227(5)	0.063(1)	−0.0019(5)	0.0023(9)	−0.0011(8)

Experimental details

H atoms were located in the difference Fourier map, but refined with fixed individual displacement parameters, using a riding mode with C—H distances of 0.93 Å (for aromatic rings), 0.96 Å (for CH_3), with U_{iso}(H) values of 1.2U_{eq}(C) (for CH in aromatic), and 1.5U_{eq}(C) (for methyl group), O—H distances are 0.82 Å with U_{iso}(H) values of 1.5U_{eq}(O).

Discussion

Acylated quinones and their derivatives serve as valuable and versatile precursors for the construction of numerous biologically active natural products [3]. Various synthetic routes to such acyl quinone building blocks have been described. Common methods, such as the Friedel–Crafts acylation and the Fries rearrangement are often inefficient and require the use of corrosive reagents such as Lewis acids and acyl chlorides [4]. Recently, research has shifted towards the implementation of greener synthetic protocols throughout organic synthesis [5, 6]. One such example is the photochemical reaction between a 1,4-benzoquinone and 4-methoxybenzaldehyde, often termed the "photo Friedel-Crafts acylation", a reaction that be carried out in sunlight.

The fragments 2,5-dihydroxyphenyl and 4′-methoxyphenyl make angle of 43.5(2)°. One intramolecular hydrogen bond is observed between O(8)—H(8)···O(10) atoms. The crystal packing is stabilized by an intermolecular O—H···O hydrogen bond, between hydroxyl groups O(9)—H(9)···O^{i}(8) [symmetry code: (i) x, 1−y, z] which links the molecules into chains with graph-set notation C(8) running parallel to the b axis, further π–π stacking interactions are observed between the phenyl ring of the 2,5-dihydroxyphenyl fragment with centroid–centroid distance of 3.835 Å. All distances and angles are in the normal range.

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