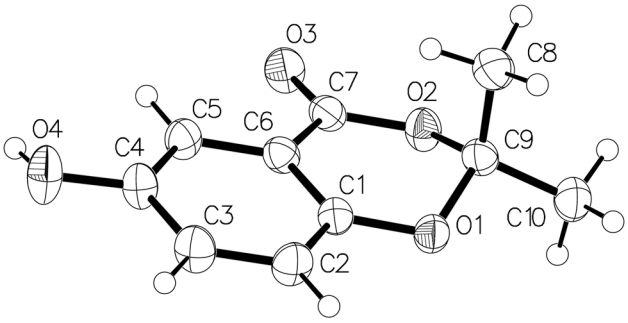
Wenqiang Tang*, Xiaona Xu, Yanrong Gao, Hongjuan Tong, Zhoujing Zhu and Bin Liu

Crystal structure of 6-hydroxy-2,2-dimethyl-4Hbenzo[d][1,3]dioxin-4-one, $C_{10}H_{10}O_4$



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Abstract

$C_{10}H_{10}O_4$, monoclinic, $P2_1/c$ (no. 14), a = 9.464(6) Å, b = 10.302(7) Å, c = 10.589(7) Å, β = 114.174(11)°, V = 941.8(10) Å^3, Z = 4, $R_{gt}(F)$ = 0.0453, $wR_{ref}(F^2)$ = 0.1394, T = 173 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:	Colorless block
Size:	0.25 × 0.15 × 0.12 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.11 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	25.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6747, 1745, 0.077
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 1430
$N(param)_{refined}$:	130
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

Source of material

The thionyl chloride (7.5 mL, 103.82 mmol) was slowly added to a solution of 2,5-dihydroxybenzoic acid (8.0 g, 51.91 mmol) in acetone (30 mL) at 0 °C with stirring under a N_2 atmosphere. The 4-dimethylaminopyridine (8.0 g, 51.91 mmol) was added and the solution was stirred at 0 °C for 1 h. The mixture was kept at room temperature for 16 h. After the reaction completion (monitored by thin-layer chromatography), the mixture was diluted with saturated $NaHCO_3$ solution and extracted with ethyl acetate. The organic layer was dried and concentrated under reduced pressure. The title compound was separated by silica-gel column chromatography using ethyl acetate/petroleum ether (10%). The target product was obtained as a white solid. The crystals were obtained by slow evaporation of mixed solution of petroleum ether and ethyl acetate (10:1, v/v) at room temperature after one week.

Experimental details

All H atoms were included using a riding model, with C–H = 0.95–0.98 Å with their U_{iso} = 1.2U_{eq} and with O–H = 0.84 Å and their U_{iso} = 1.5U_{eq}.

Comment

Heterocycles and their derivatives play significant roles in natural products and synthetic chemistry as intermediates [5, 6]. For instance, benzodioxane is an oxygen isomeric heterocyclic compound with various applications in medicine, agriculture, and synthetic chemistry [7, 8]. Among the isomers of benzodioxane, 1,3-benzodioxane and its derivatives can serve as intermediates in the chemical synthesis for pharmaceutical, natural product, and pesticide chemistry research [9–11]. Furthermore, they are potential

***Corresponding author: Wenqiang Tang**, Collaborative Innovation Center of Green Manufacturing Technology for Traditional Chinese Medicine in Shaanxi Province, School of Pharmacy, Shaanxi Institute of International Trade & Commerce, Xi'an, China,
E-mail: twqsxcq@163.com. https://orcid.org/0000-0001-5150-4549
Xiaona Xu, School of Pharmaceutical & Chemical Engineering, Xianyang Vocational Technical College, Xianyang, Shaanxi Province, China
Yanrong Gao, Hongjuan Tong, Zhoujing Zhu and Bin Liu, Collaborative Innovation Center of Green Manufacturing Technology for Traditional Chinese Medicine in Shaanxi Province, School of Pharmacy, Shaanxi Institute of International Trade & Commerce, Xi'an, China. https://orcid.org/0000-0003-2852-7739 (B. Liu)

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.31562 (17)	0.52265 (13)	0.58259 (14)	0.0282 (4)
C2	0.30498 (19)	0.44095 (14)	0.68240 (15)	0.0351 (4)
H2	0.328459	0.472000	0.773267	0.042*
C3	0.25983 (19)	0.31403 (15)	0.64773 (15)	0.0367 (4)
H3	0.254006	0.257258	0.716136	0.044*
C4	0.22242 (18)	0.26707 (14)	0.51400 (15)	0.0321 (4)
C5	0.23322 (18)	0.34836 (13)	0.41527 (15)	0.0301 (4)
H5	0.207936	0.317576	0.324001	0.036*
C6	0.28166 (16)	0.47653 (13)	0.45022 (13)	0.0273 (4)
C7	0.30899 (16)	0.56230 (13)	0.35136 (14)	0.0277 (4)
C8	0.14348 (18)	0.76360 (15)	0.45187 (15)	0.0372 (4)
H8A	0.087107	0.681107	0.427801	0.056*
H8B	0.111140	0.818796	0.369422	0.056*
H8C	0.120682	0.807590	0.523447	0.056*
C9	0.31532 (17)	0.73786 (13)	0.50570 (14)	0.0286 (4)
C10	0.4155 (2)	0.85627 (14)	0.55551 (17)	0.0379 (4)
H10A	0.400708	0.894287	0.634049	0.057*
H10B	0.386848	0.919938	0.480353	0.057*
H10C	0.524441	0.831828	0.584623	0.057*
O1	0.36664 (12)	0.64789 (9)	0.61812 (9)	0.0318 (3)
O2	0.34939 (12)	0.68546 (9)	0.39268 (9)	0.0317 (3)
O3	0.30478 (12)	0.52798 (9)	0.24067 (10)	0.0360 (3)
O4	0.17591 (15)	0.14061 (10)	0.48902 (12)	0.0437 (4)
H4	0.178817	0.116393	0.414378	0.066*

synthetic intermediates in multistep organic synthesis. Among various 1,3-benzodioxane derivatives, 4*H*-benzo[*d*][1,3]dioxin-4-one and its derivatives have been identified in nucleoside transport inhibitors, biologically active molecules such as isomerase I inhibitors, anti-plasma parasite, and cytotoxic drugs, insecticides, crop protection agents, and fungicides [12–14]. Up to date, a significant number of 4*H*-benzo[*d*][1,3]dioxin-4-one derivatives have been reported [15–24]. This paper reports the synthesis and crystal structure of a novel 4*H*-benzo[*d*][1,3]dioxin-4-one derivative compound.

The asymmetric unit contains one molecule of the title compound, where two methyl groups and one hydroxyl group replace the hydrogen atom on the 4*H*-benzo[*d*][1,3]dioxin-4-one configuration (see the Figure). The bond lengths of C9–C8, C9–C10, and C4–O4 are 1.510(3) Å, 1.502(3) Å, and 1.366(2) Å, respectively. The C–C bond lengths of the benzo moiety are in the range of 1.376(3)–1.398(3) Å, and the C–C–C angles are in the range of 118.96(15)–121.37(16)°, indicating the substitution of functional groups did not significantly change the structure. The dihedral angle of the almost flat moiety: C1···C7, O1, and O2 and the plane (C9, O1, and O2) is 43.86°. And the dihedral angle of the plane A (C9, O1, and O2) and the plane B (C8, C9, and C10) is 90.63°. The only intermolecular O4–H4···O3 hydrogen bond is observed. The O4–H4 and O3–H4 bond lengths are 0.8399(15) Å and 1.9385(16) Å. The molecule's structure is similar to the configurations of the compounds reported in the references [15, 16, 22, 24].

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