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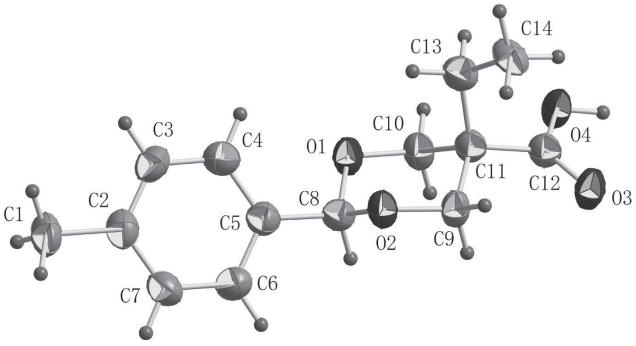
Crystal structure of 5-ethyl-2-(*p*-tolyl)-1,3-dioxane-5-carboxylic acid, $C_{14}H_{18}O_4$



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Abstract

$C_{14}H_{18}O_4$, monoclinic, $P2_1/n$ (no. 14), $a = 10.763(6)$ Å, $b = 5.941(4)$ Å, $c = 20.310(12)$ Å, $\beta = 92.238(6)°$, $V = 1297.7(13)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0484$, $wR_{ref}(F^2) = 0.1351$, $T = 296(2)$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

The mixture of 2,2-bis(hydroxymethyl)butanoic acid (1.48 g, 10.0 mmol), 4-methylbenzaldehyde (1.20 g, 10.0 mmol), cyclohexane (18 mL), *N*,*N*-dimethylformamide (5 mL) and *p*-toluenesulfonic acid (0.12 g, 0.70 mmol) was refluxed with stirring for 3 h. The solvent was evaporated under reduced pressure and then ethyl acetate was added to dissolve the residue. The solution was washed with brine (15 mL*2) and water (15 mL*2), respectively. Then the organic layer was

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.22 × 0.21 × 0.20 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.9 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{max}$, completeness:	50°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13878, 2273, 0.017
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2041
$N(param)_{refined}$:	168
Programs:	SHELX [1], Bruker programs [2]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.7278(2)	0.2095(4)	0.15164(11)	0.0745(6)
H1A	0.7796	0.1136	0.1791	0.112*
H1B	0.7782	0.3222	0.1318	0.112*
H1C	0.6866	0.1212	0.1178	0.112*
C2	0.63232(15)	0.3216(3)	0.19279(8)	0.0499(4)
C3	0.58906(16)	0.2175(3)	0.24834(9)	0.0512(4)
H3	0.6217	0.0785	0.2610	0.061*
C4	0.49848(15)	0.3151(3)	0.28548(8)	0.0462(4)
H4A	0.4705	0.2408	0.3224	0.055*
C5	0.44937(14)	0.5226(3)	0.26801(7)	0.0398(4)
C6	0.49284(16)	0.6280(3)	0.21272(8)	0.0497(4)
H6	0.4610	0.7679	0.2002	0.060*
C7	0.58265(17)	0.5285(3)	0.17594(9)	0.0552(5)
H7	0.6104	0.6026	0.1389	0.066*
C8	0.35259(14)	0.6356(3)	0.30724(7)	0.0416(4)
H8	0.2982	0.7251	0.2776	0.050*
C9	0.32269(15)	0.8987(3)	0.39092(9)	0.0490(4)
H9A	0.2710	0.9906	0.3614	0.059*
H9B	0.3653	0.9975	0.4224	0.059*
C10	0.18593(15)	0.5720(3)	0.37551(9)	0.0485(4)
H10A	0.1399	0.4548	0.3972	0.058*
H10B	0.1285	0.6528	0.3461	0.058*
C11	0.24163(13)	0.7340(3)	0.42715(7)	0.0399(4)
C12	0.13701(14)	0.8566(3)	0.45894(8)	0.0425(4)
C13	0.31437(18)	0.5956(4)	0.48010(9)	0.0603(5)
H13A	0.2593	0.4814	0.4967	0.072*
H13B	0.3818	0.5185	0.4592	0.072*
C14	0.3677(2)	0.7264(6)	0.53736(11)	0.0918(8)
H14A	0.4239	0.8384	0.5219	0.138*
H14B	0.4118	0.6263	0.5671	0.138*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H14C	0.3017	0.7986	0.5598	0.138*
H4	−0.013(3)	0.806(5)	0.4973(14)	0.102(8)*
O1	0.28147(10)	0.47264(19)	0.33843(6)	0.0502(3)
O2	0.41187(10)	0.77926(19)	0.35404(6)	0.0481(3)
O3	0.13556(11)	1.0591(2)	0.46688(7)	0.0591(4)
O4	0.04897(13)	0.7255(2)	0.47766(8)	0.0717(5)

dried with anhydrous sodium sulfate, filtered and evaporated, and the product was recrystallized from ethyl acetate to afford colorless crystals (1.80 g, yield 72%).

Experimental details

All hydrogen atoms were identified in difference Fourier syntheses. The methyl groups were idealized and refined using rigid groups allowed to rotate about the C—C bond (AFIX 137 option of the SHELXL-2013 program). The U_{iso} values of the hydrogen atoms of methyl groups were set to $1.5U_{eq}$(C) and the U_{iso} values of all other hydrogen atons were set to $1.2U_{eq}$(C).

Comment

As protected intermediates, ketal compounds have a wide application in organic syntheses [3, 4]. Some of these compounds have insecticidal as well as anti-foaming properties [5]. In addition, the title crystal structure is similar to 1,3-dioxans [6]. One molecule of the title compound forms the asymmetric unit. The bond lengths and angles are in the expected ranges. Especially the configuration at C8 and C11 was determined.

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