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Crystal structure of 2-(2-bromophenyl)-5-ethyl-1,3-dioxane-5-carboxylic acid, $C_{13}H_{15}BrO_4$

DOI 10.1515/ncrs-2016-0136

Received April 24, 2016; accepted August 26, 2016; available online September 17, 2016

Abstract

$C_{13}H_{15}BrO_4$, orthorhombic, *Pbca* (no. 61), $a = 15.894(3)$ Å, $b = 7.6064(16)$ Å, $c = 21.571(4)$ Å, $V = 2607.8(9)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0268$, $wR_{\text{ref}}(F^2) = 0.0702$, $T = 296(2)$ K.

CCDC no.: 1500923

The asymmetric unit of the tilted 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 material

The mixture of 2,2-bis(hydroxymethyl)butyric acid (1.92 g, 13 mmol), 2-bromobenzaldehyde (2.21 g, 12 mmol), cyclohexane (15 mL), *N,N*-dimethylformamide (5 mL) and *p*-toluene sulfonic acid (0.13 g, 0.75 mmol) were refluxed with stirring for 5 h. After the mixture was cooled, sodium bicarbonate (0.06 g, 0.76 mmol) was added to neutralize the mixture and stirred at room temperature for 1 h. The solvent was evaporated under reduced pressure and then ethyl acetate was

Table 1: Data collection and handling.

Crystal:	Colourless blocks
	Size $0.38 \times 0.32 \times 0.29$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	31.6 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{\text{max}}$, completeness:	50° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	22782, 2276, 0.030
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1970
$N(\text{param})_{\text{refined}}$:	165
Programs:	SHELX [8, 9], Bruker programs [10]

added to dissolve the residue. Subsequently, the solution was washed with brine (25 mL $\times$ 2) and water (25 mL $\times$ 2). Then the organic layer was dried with anhydrous sodium sulfate, filtered and evaporated. The product was recrystallized from ethyl acetate to afford crystals (2.84 g, yield 75%).

Experimental details

All hydrogen atoms were identified in difference Fourier synthesis. The methyl group and hydroxyl group were idealized and refined using rigid groups allowed to rotate about the C—C bond and O—C bond (AFIX 137 option of the SHELXL-2013 program [9]). All other H atoms were positioned geometrically. The U_{iso} values of the hydrogen atoms of methyl group and hydroxyl group were set to $1.5U_{\text{eq}}(\text{C})$ and the U_{iso} values of all other hydrogen atoms were set to $1.2U_{\text{eq}}(\text{C})$. Some non-fitting low-order reflections were omitted.

Discussion

Ketal compounds have a wide application in organic syntheses, that is because they are commonly used as a protection of carbonyl groups [1]. In addition, this type of compounds have insecticidal as well as anti-foaming properties [2, 3]. The crystal structures of some similar 1,3-dioxanes have been reported [4–7]. The new compound 2-(2-bromophenyl)-5-ethyl-1,3-dioxane-5-carboxylic acid was synthesized by the reaction of 2,2-bis(hydroxymethyl)-butyric acid with 2-bromobenzaldehyde, with *p*-toluene sulfonic acid as catalyst, and its structure was determined by single-crystal X-ray structure analysis [8].

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.073583(17)	0.12760(3)	0.338058(11)	0.05051(12)
O4	0.14606(9)	0.13521(17)	0.19368(6)	0.0327(3)
O3	0.07651(9)	−0.08743(18)	0.14157(7)	0.0326(3)
C8	0.11771(12)	−0.1296(2)	0.24636(9)	0.0283(4)
C13	0.11829(12)	−0.0887(3)	0.30924(9)	0.0307(4)
O2	−0.00822(9)	0.29548(19)	0.02122(7)	0.0412(4)
C11	0.17919(15)	−0.3666(3)	0.33388(11)	0.0427(6)
H11	0.2000	−0.4455	0.3630	0.051*
C4	0.05808(13)	0.3237(3)	0.04761(9)	0.0302(4)
O1	0.09792(10)	0.4740(2)	0.04454(8)	0.0482(4)
H1	0.0703	0.5437	0.0240	0.072*
C9	0.14818(13)	−0.2935(3)	0.22891(10)	0.0349(5)
H9	0.1482	−0.3243	0.1872	0.042*
C5	0.11744(14)	0.2674(3)	0.15200(9)	0.0332(5)
H5A	0.1591	0.3601	0.1491	0.040*
H5B	0.0656	0.3184	0.1675	0.040*
C3	0.10215(12)	0.1879(3)	0.08747(9)	0.0280(4)
C2	0.18663(14)	0.1361(3)	0.05808(10)	0.0372(5)
H2A	0.2233	0.2381	0.0586	0.045*
H2B	0.2126	0.0466	0.0838	0.045*
C6	0.04309(13)	0.0299(3)	0.09604(9)	0.0322(4)
H6A	−0.0120	0.0707	0.1091	0.039*
H6B	0.0367	−0.0315	0.0569	0.039*
C7	0.08622(12)	−0.0016(3)	0.19868(9)	0.0295(4)
H7	0.0320	0.0469	0.2120	0.035*
C10	0.17844(14)	−0.4120(3)	0.27221(11)	0.0409(5)
H10	0.1981	−0.5215	0.2597	0.049*
C12	0.14935(14)	−0.2051(3)	0.35289(10)	0.0391(5)
H12	0.1501	−0.1747	0.3947	0.047*
C1	0.18201(18)	0.0676(4)	−0.00749(12)	0.0609(7)
H1A	0.1600	0.1576	−0.0342	0.091*
H1B	0.1457	−0.0333	−0.0088	0.091*
H1C	0.2373	0.0348	−0.0212	0.091*

All bond lengths are in the expected ranges. Hydrogen bonds connect adjacent acid molecules pairwise. The

formation of such hydrogen bonded dimers is ubiquitously found in the structural chemistry of carboxylic acids.

Acknowledgements: This work was financially supported by the Science and Technology Planning Project of Hunan Province (2015GK3037), the Scientific Research Fund of Hunan Provincial Education Department (14A058, 16B104).

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