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Crystal structure of 2-(2-bromophenyl)-5-methyl-1,3-dioxane-5-carboxylic acid, C$_{12}$H$_{13}$BrO$_4$

Abstract
C$_{12}$H$_{14}$BrO$_4$, monoclinic, $P2_1/n$, $a = 9.599(2)$ Å, $b = 14.399(3)$ Å, $c = 9.2361(19)$ Å, $\beta = 100.182(2)$°, $V = 1256.5(5)$ Å$^3$, $Z = 4$, $R_{gt}(F) = 0.0285$, $wR_{ref}(F^2) = 0.0779$, $T = 296(2)$ K.

Table 1: Data collection and handling.

| Crystal: | Colourless blocks |
| Wavelength: | Mo Ka radiation (0.71073 Å) |
| $\mu$: | 32.7 cm$^{-1}$ |
| Diffractometer, scan mode: | Bruker APEX-II, $\phi$ and $\omega$ |
| $2\theta_{max}$, completeness: | 55°, >99% |
| $N(hkl)_{measured}, N(hkl)_{unique}, R_{int}$: | 11656, 2212, 0.027 |
| Criterion for $I_{obs}, N(hkl)_{gt}$: | $I_{obs} > 2 \sigma(I_{obs}), 1985$ |
| $N(param)_{refined}$: | 159 |
| Programs: | Bruker programs [7], SHELX [8] |

The asymmetric unit of the 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)propionic acid (1.88 g, 14.0 mmol), 2-bromobenzaldehyde (2.21 g, 12.0 mmol), cyclohexane (18 mL), N,N-dimethylformamide (5 mL) and $p$-toluenesulfonic acid (0.12 g, 0.70 mmol) were refluxed with stirring for three hours. After the mixture was cooled, sodium bicarbonate (0.06 g, 0.76 mmol) was added to neutralize $p$-toluene sulfonic acid and stirred at room temperature for 40 min. The solvent was evaporated under reduced pressure and ethyl acetate was added to dissolve the residue. The solution was washed with saturated salt water (15 mL × 2) and water (15 mL × 2), respectively. Then the organic layer was dried with anhydrous sodium sulfate, filtered and evaporated. The product was recrystallized from ethyl acetate to afford colorless crystals (2.9 g, 9.6 mmol; yield 80%).

Experimental details
All hydrogen atoms were identified in difference Fourier synthesis. The methyl group was idealized and allowed to rotate about the C—C bond (AFIX 137 option of the SHELXL program [8]). The $U_{eq}$ values of the hydrogen atoms of methyl groups were set to 1.5$U_{eq}$(C) and the $U_{eq}$ values of all other hydrogen atoms were set to 1.2$U_{eq}$(C).

Discussion
Ketal compounds have a wide application in organic syntheses, because they are commonly used as a protection of carbonyl groups or intermediates [1]. In addition, these compounds have insecticidal as well as anti-foaming properties [2, 3]. The crystal structures of some similar 1,3-dioxanes have been reported [4–6]. The new compound 2-(2-bromophenyl)-5-methyl-1,3-dioxane-5-carboxylic acid was synthesized by...
the reaction of 2,2-bis(hydroxymethyl)propionic acid with 2-bromobenzaldehyde with p-toluene sulfonic acid as catalyst, DMF and cyclohexane as solvent, and its structure was studied by single-crystal X-ray structure analysis [7]. All structural parameters are in the expected ranges. Two adjacent title molecules are pairwise connected by OH···O hydrogen bonds.

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References


