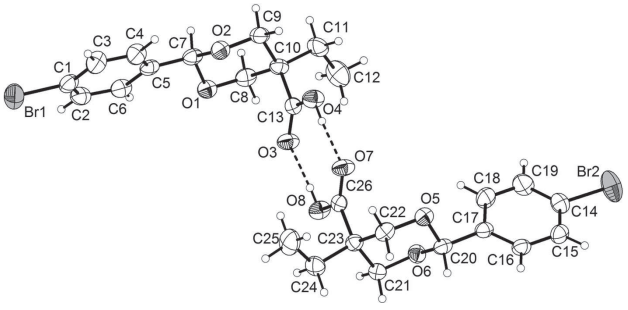
**Open Access**

Guo-Kai Jia, Lin Yuan, Min Zhang and Xian-You Yuan*

# Crystal structure of 2-(4-Bromophenyl)-5-ethyl-1,3-dioxane-5-carboxylic acid, $C_{13}H_{15}BrO_4$




DOI 10.1515/ncrs-2016-0021
Received January 13, 2016; accepted April 17, 2016; available online May 6, 2016

## Abstract

$C_{13}H_{15}BrO_4$, monoclinic, $P2_1/n$ (no. 14), $a = 12.872(4)$ Å, $b = 8.311(2)$ Å, $c = 24.598(7)$ Å, $\beta = 92.556(3)°$, $V = 2629.0(13)$ Å$^3$, $Z = 8$, $R_{gt}(F) = 0.0357$, $wR_{ref}(F^2) = 0.0932$, $T = 296(2)$ K.

**CCDC no.:** 1474710

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 (2.01 g, 13.50 mmol), 4-bromobenzaldehyde (4.43 g, 12.26 mmol), cyclohexane (20 mL), N,N-dimethylformamide (6 mL) and *p*-toluene sulfonic acid (0.13 g, 0.75 mmol) were refluxed for 3 h. After the mixture was cooled, sodium bicarbonate (0.06 g, 0.76 mmol) was added and stirred at room temperature for half an hour. The solvent was evaporated under reduced pressure and then ethyl acetate was added to dissolve the residue. Subsequently, the solution was washed with brine

***Corresponding author: Xian-You Yuan,** College of Chemistry and Bioengineering, Hunan University of Science and Engineering, Yongzhou, Hunan 425199, P. R. China, e-mail: yuanxianzhangmin@163.com
**Guo-Kai Jia, Lin Yuan and Min Zhang:** College of Chemistry and Bioengineering, Hunan University of Science and Engineering, Yongzhou, Hunan 425199, P. R. China

**Table 1:** Data collection and handling.

| | |
|---|---|
| Crystal: | Colorless blocks size 0.43 × 0.37 × 0.32 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 31.31 cm$^{-1}$ |
| Diffractometer, scan mode: | Bruker Apex-II CCD, $\varphi$ and $\omega$ |
| $2\theta_{max}$, completeness | 53.4°, >99%, |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$, $R_{int}$: | 27785, 4613, 0.033 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\,\sigma(I_{obs})$, 3860 |
| $N(param)_{refined}$: | 328 |
| Programs: | Bruker programs [10], SHELX [11] |

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

| Atom | x | y | z | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Br2 | 1.61659(3) | 0.37502(5) | 0.133099(13) | 0.07253(15) |
| Br1 | 0.13350(2) | 0.72644(5) | 0.103814(16) | 0.07055(14) |
| C26 | 0.93542(17) | 0.3361(3) | 0.17355(9) | 0.0308(5) |
| C7 | 0.5835(2) | 0.8453(3) | 0.03997(10) | 0.0390(6) |
| H7 | 0.5815(2) | 0.9342(3) | 0.01378(10) | 0.0468(7)* |
| C13 | 0.83030(18) | 0.6693(3) | 0.07657(9) | 0.0321(5) |
| C14 | 1.4856(2) | 0.3238(3) | 0.16068(10) | 0.0421(6) |
| C23 | 0.96966(19) | 0.2004(3) | 0.21137(9) | 0.0346(5) |
| C10 | 0.7990(2) | 0.8034(3) | 0.03775(10) | 0.0364(5) |
| C4 | 0.4365(2) | 0.8849(3) | 0.10218(11) | 0.0468(7) |
| H4 | 0.4797(2) | 0.9511(3) | 0.12369(11) | 0.0562(8)* |
| C15 | 1.4800(2) | 0.2256(3) | 0.20544(11) | 0.0426(6) |
| H15 | 1.5403(2) | 0.1880(3) | 0.22342(11) | 0.0512(7)* |
| C22 | 1.0400(2) | 0.2626(3) | 0.25812(9) | 0.0387(6) |
| H22a | 1.0067(2) | 0.3533(3) | 0.27507(9) | 0.0464(7)* |
| H22b | 1.0495(2) | 0.1786(3) | 0.28529(9) | 0.0464(7)* |
| C21 | 1.03131(19) | 0.0744(3) | 0.18103(11) | 0.0387(6) |
| H21a | 1.04116(19) | −0.0202(3) | 0.20375(11) | 0.0465(7)* |
| H21b | 0.99216(19) | 0.0426(3) | 0.14817(11) | 0.0465(7)* |
| C8 | 0.7218(2) | 0.7436(3) | −0.00645(10) | 0.0410(6) |
| H8a | 0.7133(2) | 0.8250(3) | −0.03454(10) | 0.0492(7)* |
| H8b | 0.7492(2) | 0.6474(3) | −0.02297(10) | 0.0492(7)* |
| C9 | 0.7465(2) | 0.9393(3) | 0.06847(11) | 0.0433(6) |
| H9a | 0.7900(2) | 0.9693(3) | 0.10005(11) | 0.0519(7)* |
| H9b | 0.7388(2) | 1.0328(3) | 0.04503(11) | 0.0519(7)* |
| C11 | 0.8981(2) | 0.8668(3) | 0.01230(12) | 0.0509(7) |
| H11a | 0.8798(2) | 0.9603(3) | −0.00970(12) | 0.0610(8)* |
| H11b | 0.9462(2) | 0.9020(3) | 0.04137(12) | 0.0610(8)* |
| C24 | 0.8704(2) | 0.1210(3) | 0.23209(11) | 0.0470(7) |
| H24a | 0.8293(2) | 0.0809(3) | 0.20095(11) | 0.0564(8)* |

**Table 2** (continued)

| Atom | x | y | z | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| H24b | 0.8908(2) | 0.0289(3) | 0.25435(11) | 0.0564(8)* |
| C16 | 1.3832(2) | 0.1833(3) | 0.22332(10) | 0.0389(6) |
| H16 | 1.3787(2) | 0.1164(3) | 0.25341(10) | 0.0466(7)* |
| C20 | 1.18926(19) | 0.1839(3) | 0.21395(10) | 0.0372(6) |
| H20 | 1.19792(19) | 0.0926(3) | 0.23896(10) | 0.0446(7)* |
| C17 | 1.2934(2) | 0.2393(3) | 0.19706(10) | 0.0356(5) |
| C6 | 0.4088(2) | 0.7184(3) | 0.02404(10) | 0.0426(6) |
| H6 | 0.4334(2) | 0.6698(3) | −0.00690(10) | 0.0511(7)* |
| C5 | 0.4749(2) | 0.8125(3) | 0.05655(10) | 0.0369(6) |
| C3 | 0.3356(2) | 0.8607(4) | 0.11619(12) | 0.0518(7) |
| H3 | 0.3109(2) | 0.9083(4) | 0.14731(12) | 0.0622(9)* |
| C2 | 0.3065(2) | 0.6960(3) | 0.03709(11) | 0.0462(7) |
| H2 | 0.2618(2) | 0.6349(3) | 0.01466(11) | 0.0554(8)* |
| C18 | 1.3019(2) | 0.3434(4) | 0.15336(11) | 0.0505(7) |
| H18 | 1.2420(2) | 0.3853(4) | 0.13617(11) | 0.0605(8)* |
| C19 | 1.3970(2) | 0.3851(4) | 0.13524(11) | 0.0529(7) |
| H19 | 1.4017(2) | 0.4547(4) | 0.10584(11) | 0.0635(9)* |
| C1 | 0.2716(2) | 0.7653(3) | 0.08369(11) | 0.0449(6) |
| C25 | 0.8023(2) | 0.2287(5) | 0.26484(14) | 0.0670(9) |
| H25a | 0.8404(7) | 0.264(2) | 0.2972(5) | 0.1004(14)* |
| H25b | 0.7815(16) | 0.3207(15) | 0.2434(4) | 0.1004(14)* |
| H25c | 0.7417(10) | 0.1702(10) | 0.2748(8) | 0.1004(14)* |
| C12 | 0.9531(3) | 0.7475(5) | −0.02261(14) | 0.0690(10) |
| H12a | 0.9665(18) | 0.6505(12) | −0.0023(4) | 0.1035(14)* |
| H12b | 0.9102(9) | 0.724(2) | −0.0545(5) | 0.1035(14)* |
| H12c | 1.0178(10) | 0.7927(13) | −0.0332(9) | 0.1035(14)* |
| O5 | 1.13900(13) | 0.3113(2) | 0.24020(7) | 0.0382(4) |
| O7 | 0.94367(15) | 0.4784(2) | 0.18635(7) | 0.0468(5) |
| O4 | 0.87465(16) | 0.7165(2) | 0.12221(7) | 0.0467(5) |
| H4a | 0.895(2) | 0.6378(3) | 0.1399(6) | 0.0701(7)* |
| O1 | 0.62330(14) | 0.7084(2) | 0.01460(7) | 0.0395(4) |
| O3 | 0.81976(15) | 0.5263(2) | 0.06459(7) | 0.0452(4) |
| O6 | 1.13047(13) | 0.1355(2) | 0.16701(7) | 0.0389(4) |
| O2 | 0.64706(13) | 0.8905(2) | 0.08546(7) | 0.0413(4) |
| O8 | 0.89221(15) | 0.2891(2) | 0.12772(7) | 0.0441(4) |
| H8 | 0.870(2) | 0.3674(4) | 0.1107(6) | 0.0662(7)* |

(20 ml×2) and water (20 ml×2), respectively. Then the organic layer was dried with anhydrous sodium sulfate, filtered. The product was recrystallized from n-hexane to afford colorless crystals (4.9 g, 9.98 mmol; yield 81.42 %).

## Experimental details

Carbon-bound H atoms were placed in calculated positions (C—H 0.95 Å) and were included in the refinement in the riding model approximation, with $U$(H) set to 1.2$U_{eq}$(C). The H atoms of the methyl group were allowed to rotate with a fixed angle around the C—C bond to best fit the experimental electron density, with $U$(H) set to 1.5$U_{eq}$(O). The H atoms of the hydroxyl groups were refined using the HFIX 147 option in the SHELX program suite [11], with $U$(H) set to 1.5$U_{eq}$(O).

## Discussion

Ketal compounds have a wide application in organic syntheses, because they are used as a protection of carbonyl groups or intermediates [1, 2]. In addtition, this type of compounds has insecticidal as well as anti-foaming properties [3, 4]. The crystal structures of some similar 1,3-dioxanes have been reported [5–9]. There are two crystallographically independent molecules in the asymmetric unit. They are pairwise hydrogen bonded to form dimeric units (cf. the figure). All bond lengths and angles are in the expected ranges.

**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, 13A030).

## References

1. Ono, D.; Yamamura, S.; Nakamura, M.: Preparation and properties of bis (sodium sulfate) types of cleavable surfactants derived from diethyl tartrate. J. Oleo. Sci. **54** (2005) 51–57.
2. Marrian, S. F.: The chemical reactions of pentaerythritol and its derivatives. Chem. Rev. **43** (1948) 149–198.
3. Wang, G. W.; Yuan, X. Y.; Liu, Y. C.; Lei, X.G.: Preparation and properties of sulfonate salt-type cleavable surfactants with a 1,3-dioxane ring. J. Am. Oil Chem. Soc. **71** (1994) 727–730.
4. Yuan, X.Y.; Yang, N.F.; Luo, H.A.; Liu, Y.J.: Synthesis of hetero iacetals and diketals of pentaerythritol under microwave irradiation. Chin. J. Org. Chem. **25** (2005) 1049–1052.
5. Yuan, L.; Ou, G. C.; Shi, J. H.; Zhang, M.; Yuan, X. Y.: Synthesis and crystal structure of 12-(2-chlorophenyl)-7,11,13,16-tetraoxaspiro [5.2.5.2]cetane. Chin. J. Org. Chem. **33** (2013) 1817–1821.
6. Godard, A.; Thiebaud-Roux, S.; De Caro, P.; Vedrenne, E.; Mouloungui, Z.: New one-pot syntheses of ketals and acetals from oleic acid. Industrial Crops and Products. **52** (2014) 111–117.
7. Jia, G. K.; Yuan, L.; Zhang, M.; Yuan, X. Y.: 2-(2-Chlorophenyl)-5-methyl-1,3-dioxane-5-carboxylic acid. Acta Crystallogr. **E68** (2012) o2037.
8. Zhang, M.; Jia, G. K.; Yuan, L.; Yuan, X. Y.: Crystal structure of 2- (4-chlorophenyl)-5-methyl-1, 3-dioxane-5-carboxylic acid, $C_{12}H_{13}ClO_4$. Z. Kristallogr. NCS **228** (2013) 393–394.
9. Yuan, L.; Shi J. H.; Zhang M.: Crystal structure of 3, 3-dihydroxymethyl-1,6-dioxa-spiro[5.5]undecane, $C_{11}H_{20}O_4$. Z. Kristallogr. NCS **227** (2012) 35–36.
10. Bruker: SAINT-Plus, SHELXTL and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, 2004.
11. Sheldrick, G. M.: A short history of *SHELX*. Acta Crystallogr. **A64** (2008) 112–122.