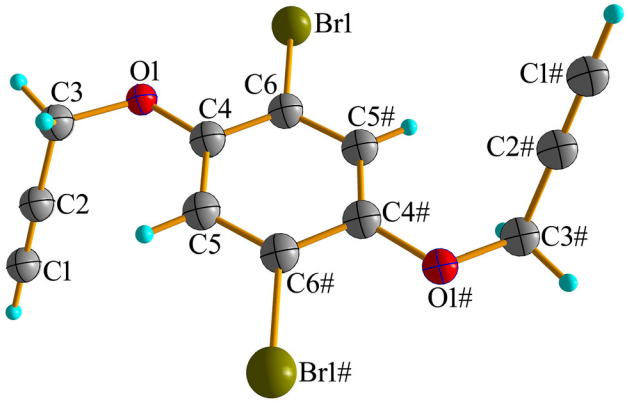
Zhi-Yong Wang, Qi-Long Zhang*, Xiu-Ming Zhang, Xu Zhou, Xian-Jiong Yang and Hong Xu

Crystal structure of 1,4-dibromo-2,5-bis(prop-2-yn-1-yloxy)benzene, $C_{12}H_8Br_2O_2$



https://doi.org/10.1515/ncrs-2023-0401
Received September 10, 2023; accepted October 13, 2023;
published online October 23, 2023

Abstract

$C_{12}H_8Br_2O_2$, monoclinic, $P2_1/c$ (no. 14), a = 4.1957(13) Å, b = 13.402(4) Å, c = 11.160(3) Å, β = 99.645(10)°, V = 618.7(3) Å^3, Z = 2, $R_{gt}(F)$ = 0.0287, $wR_{ref}(F^2)$ = 0.0701, T = 273(2) K.

CCDC no.: 2301074

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:	Colourless block
Size:	0.18 × 0.17 × 0.13 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	6.53 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	28.2°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6207, 1503, 0.043
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 1120
$N(param)_{refined}$:	73
Programs:	Olex2 [1], Bruker [2], SHELX [3], Diamond [4]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.98931 (7)	0.46954 (2)	0.75639 (2)	0.04303 (13)
O1	0.6210 (5)	0.65299 (14)	0.66838 (17)	0.0406 (5)
C1	0.6053 (10)	0.8509 (3)	0.4731 (3)	0.0702 (11)
H1	0.6648	0.8885	0.4103	0.084*
C2	0.5314 (8)	0.8043 (2)	0.5510 (3)	0.0468 (7)
C3	0.4427 (8)	0.7443 (2)	0.6493 (3)	0.0432 (7)
H3A	0.4798	0.7830	0.7238	0.052*
H3B	0.2137	0.7290	0.6309	0.052*
C4	0.5531 (6)	0.5795 (2)	0.5825 (2)	0.0311 (6)
C5	0.3405 (6)	0.5896 (2)	0.4736 (2)	0.0325 (6)
H5	0.2317	0.6495	0.4550	0.039*
C6	0.7098 (6)	0.4891 (2)	0.6074 (2)	0.0309 (6)

1 Source of materials

In a round bottomed flask, add 2,5–dibromobenzene-1,4-diol (0.267 g, 1 mmol), 2–bromoethyl metal ether (0.590 g, 5 mmol), K_2CO_3(0.267 g, 2 mmol), and 30 mL of N,N-dimethylformamide. React at 105 °C for 68 h, cool, filter to remove K_2CO_3, reduce pressure distillation to remove solvent, separate by column chromatography, and use dichloromethane and petroleum ether as eluents to obtain a white solid. Dissolve a small amount of solid in ethanol and let it evaporate for 9 days before growing crystals.

2 Experimental details

Crystal data, data collection and structure refinement details are summarized in Table 1. Using Olex2 [1], the structure was solved using Charge Flipping and refined with the ShelXL [3] refinement. All hydrogen atoms were positioned geometrically, with the d(C–H) = 0.97–0.99 Å, U_{iso}(H) = 1.2 times U_{eq}(C) and U_{iso}(H) = 1.5 times U_{eq}(O).

***Corresponding author: Qi-Long Zhang**, School of Basic Medical Science, Guizhou Medical University, Guiyang, 550025, People's Republic of China, E-mail: sciqlzhang@gmc.edu.cn. https://orcid.org/0000-0002-6715-9548
Zhi-Yong Wang, Xiu-Ming Zhang, Xu Zhou, Xian-Jiong Yang and Hong Xu, School of Basic Medical Science, Guizhou Medical University, Guiyang, 550025, People's Republic of China

3 Comment

The bromine atom of dibromobenzene is easily reacted with vinyl pyridine to form compounds with large conjugated structures, which have excellent luminescent properties and are therefore favored by researchers [5]. Click chemistry has been well applied in many fields such as drug development and biomedical materials [6], and the reaction of copper catalyzed azides forming 5-membered heteroatomic rings with alkynes is one of the classic click reactions [7]. The modification of alkynyl groups on the benzene ring provides a basis for the click reaction. We synthesized compound 1,4-dibromo-2,5-bis(prop-2-yn-1-yloxy) benzene using the reaction of 2,5-dibromobenzene-1,4-diol and propylene bromide. The asymmetric unit of the title compound, $C_{12}H_8Br_2O_2$, contains one half molecule located around an inversion center. The orientation of the two alkyne groups is opposite, located above and below the benzene ring, with C3–O1–C4–C5 torsion angles of 5.02(0.36)°. Bond lengths and angles are in the expected ranges [8, 9].

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: This work was supported by the Science and Technology Foundation of Guizhou Province (grant number ZK[2022]395, 19NSP042, 26222030209), the Provincial General Project of University Student Innovation and Entrepreneurship Fund, China (No. 202210660045).
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* 2009, *42*, 339–341.
2. Bruker. *APEX2, SAINT and SADABS*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2012.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Brandenburg K. *DIAMOND. Visual Crystal Structure Information System. Ver. 4.0*; Crystal Impact: Bonn, Germany, 2015.
5. Gong X., Zhang Q., Zhang S., Xia Y., Bai Q. H., Chen S. Y., Ni X. L. A cationic fluorescent probe for BF_4^- and PF_6^- anions by aggregation self-assembly: an efficient approach to recognition of anions in aqueous solution. *Dyes Pigments* 2019, *163*, 502–508.
6. Hu F., Qi G. B., Kenry M. D., Zhou S. W., Wu M., Wu W. B., Liu B. Visualization and in situ ablation of intracellular bacterial pathogens through metabolic labeling. *Angew. Chem., Int. Ed.* 2020, *59*, 9288–9292.
7. Mao D., Hu F., Kenry Q. G. B., Ji S. H., Wu W. B., Kong D. L., Liu B. One-step in vivo metabolic labeling as a theranostic approach for overcoming drug-resistant bacterial infections. *Mater. Horizons* 2020, *7*, 1138–1143.
8. Bolton O., Lee K., Kim H.-J., Lin K. Y., Kim J. Activating efficient phosphorescence from purely organic materials by crystal design. *Nat. Chem.* 2011, *3*, 205–210.
9. Shi H., An Z., Li P.-Z., Yin J., Xing G., He T., Chen H., Wang J., Sun H., Huang W., Zhao Y. Enhancing organic phosphorescence by manipulating heavy-atom interaction. *Cryst. Growth Des.* 2016, *16*, 808–813.