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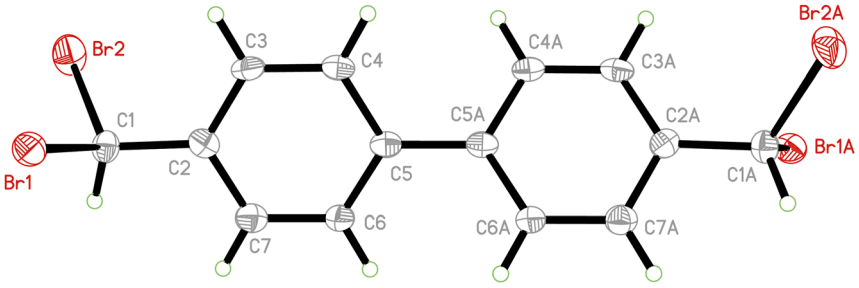
Crystal structure of 4,4′-bis(dibromomethyl)-1,1′-biphenyl, $C_{14}H_{10}Br_4$



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Abstract

$C_{14}H_{10}Br_4$, tetragonal, $P4_32_12$ (no. 96), a = 6.8288(8) Å, c = 31.988(6) Å, V = 1491.7(5) Å^3, Z = 4, $R_{gt}(F)$ = 0.0540, w$R_{ref}(F^2)$ = 0.1479, T = 193 K.

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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:	0.40 × 0.32 × 0.25 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	10.8 mm^{-1}
Diffractometer, scan mode:	Bruker Apex-II, φ and ω
θ_{max}, completeness:	27.5°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7429, 1718, 0.062
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 1,426
$N(param)_{refined}$:	83
Programs:	Bruker,[1] Shelx[2,3]

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

Atom	x	y	z	U_{iso}*/U_{eq}
Br1	1.27421 (17)	0.07779 (19)	0.44101 (4)	0.0437 (4)
Br2	0.9563 (2)	0.0867 (2)	0.36905 (4)	0.0595 (5)
C1	1.1005 (16)	0.2456 (16)	0.4080 (3)	0.036 (2)
H1A	1.1837	0.3384	0.3916	0.043*
C2	0.9693 (15)	0.3658 (14)	0.4368 (3)	0.033 (2)
C3	0.8069 (16)	0.2929 (16)	0.4564 (3)	0.035 (2)
H3A	0.7737	0.1591	0.4525	0.042*
C4	0.6902 (15)	0.4069 (17)	0.4814 (3)	0.035 (2)
H4A	0.5797	0.3507	0.4949	0.042*
C5	0.7334 (15)	0.6056 (15)	0.4872 (3)	0.031 (2)
C6	0.8961 (16)	0.6788 (16)	0.4667 (3)	0.039 (3)
H6A	0.9287	0.8131	0.4699	0.047*
C7	1.0119 (16)	0.5633 (14)	0.4417 (3)	0.039 (3)
H7A	1.1214	0.6186	0.4277	0.047*

1 Source of material

The chemical reagents 4,4′-dimethylbiphenyl, dibenzoyl peroxide and N-bromosuccinimide were purchased from Aladdin Biochemical Technology Co., Ltd without further purification. A mixture of 4,4′-dimethylbiphenyl (3.6 g, 20 mmol), N-bromosuccinimide (7.1 g 90 mmol), dibenzoyl peroxide (0.48 g, 2 mmol) and benzene (120 mL) was stirred at 80 °C for 30 min. After refluxing under nitrogen for 5 h, the solution was allowed to cool and was filtered. The organic phase was concentrated under reduced pressure, then the crude products were purified by flash column chromatography. Colorless crystals of the title compound were obtained by slow volatilization of a solution of ethanol/hexane at room temperature.

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^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.66 (d, J = 8.5 Hz, 4H), 7.58 (d, J = 8.5 Hz, 4H), 6.70 (s, 2H).

2 Experimental details

Crystallographic data collection was carried out on a Bruker Smart Apex CCD area detector diffractometer with graphite-monochromated Mo Kα radiation at 193 K.[1] The structure of the title compound was solved with the Shelxs-2014[2] software package and refined with the Shelxl-2018[3] program. Hydrogen atoms were placed in idealized positions and refined as riding atoms. The U_{iso} values were constrained to be 1.2 U_{eq} of the parent atoms. The structure was refined as an inversion twin (ratio= 0.76(7)/0.23(7)).

3 Comment

Bromine chemistry has received much attention in organic synthesis in the past decades.[4–6] Dibromomethyl aromatic derivatives are identified as being an important building block for the synthesis of aromatic imines, aromatic aldehydes, aromatic acetals and polymeric compounds.[7–10] In our research we focused on the synthesis of dibromomethyl aromatic derivatives, we have systhesized and characterized crystal structure of 1,3,5-tris(dibromomethyl)benzene in the previously work.[11]

Single-crystal structure determination revealed that the title compound crystallizes in the tetragonal system with space group $P4_32_12$. The asymmetric unit consists of half 4,4′-bis(dibromomethyl)-1,1′-biphenyl molecule. The C–Br bond lengths are in the range of 1.922(11)–1.959(10) Å and the Br–C–Br angle is 109.2(5)°, those are similar to that observed in previously reported dibromomethyl aromatic compounds, such as 1,2-bis(dibromomethyl)benzene,[12] 1,3-bis(dibromomethyl)benzene,[12] 1,4-bis(dibromomethyl)benzene[13] and 1,3,5-tris(dibromomethyl)benzene.[11] As shown in the figure, the 4,4′-bis(dibromomethyl)-1,1′-biphenyl molecule is located on a twofold axis, with dihedral angle between the two benzene rings of 27.72(4)°. The dihedral angles between the plane defined the terminal dibromomethyl group and the least-squares plane of the benzene ring are 80.99° (C1/Br1/Br2 and C2/C3/C4/C5/C6) and 63.68(6)° (C1/Br1/Br2 and $C2^i/C3^i/C4^i/C5^i/C6^i$) [symmetry codes: (i) y, x, $-z$ + 1]. The two appended dibromomethyl groups make dihedral angle of 73.52(1)°. In the solid state, the neighbor molecules are linked by weak C1–H1A…$Br1^{ii}$ and C1–H1A…$Br2^{ii}$ [symmetry codes: (ii) $-x$ + 5/2, y + 1/2, $-z$ + 3/4] hydrogen bonds.

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