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Crystal structure of 4,4'-(oxybis(methylene))bis(bromobenzene), $C_{14}H_{12}Br_2O$

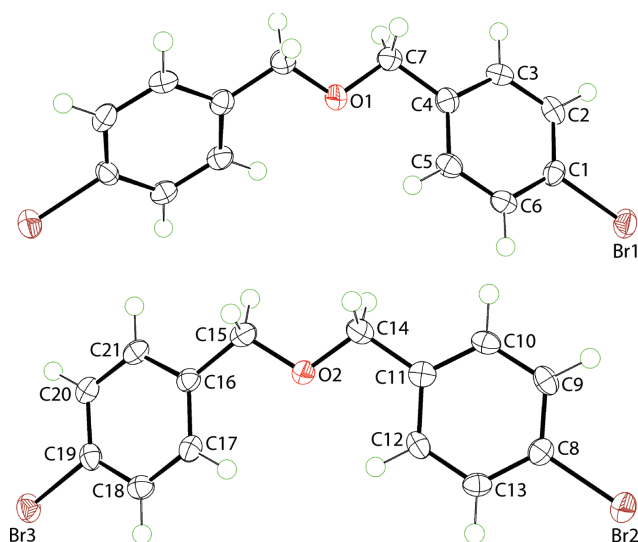


Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	$0.14 \times 0.08 \times 0.04$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	7.87 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.1° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	22804, 3289, 0.029
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3270
$N(\text{param})_{\text{refined}}$:	231
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.71041(2)	1.07282(6)	0.49566(3)	0.02286(10)
O1	0.500000	0.6195(6)	0.500000	0.0243(8)
C1	0.65770(10)	0.8905(6)	0.5020(3)	0.0171(7)
C2	0.66291(11)	0.6783(6)	0.5555(3)	0.0190(7)
H2	0.692322	0.620597	0.586411	0.023*
C3	0.62408(10)	0.5515(6)	0.5630(3)	0.0179(6)
H3	0.627095	0.405373	0.599724	0.021*
C4	0.58078(11)	0.6342(6)	0.5177(3)	0.0172(7)
C5	0.57695(11)	0.8488(6)	0.4634(3)	0.0179(7)
H5	0.547658	0.907569	0.432146	0.021*
C6	0.61544(10)	0.9773(6)	0.4546(3)	0.0180(7)
H6	0.612751	1.122309	0.416662	0.022*
C7	0.53983(10)	0.4892(6)	0.5253(3)	0.0188(7)
H7A	0.538544	0.362960	0.465956	0.023*
H7B	0.542269	0.423023	0.607969	0.023*
Br2	0.52995(2)	−0.04917(6)	0.79106(3)	0.02331(10)
Br3	0.94938(2)	−0.07311(5)	0.80258(3)	0.02156(9)
O2	0.74410(7)	0.3942(4)	0.8522(2)	0.0202(5)
C8	0.58424(10)	0.1270(6)	0.8185(3)	0.0167(7)
C9	0.58410(10)	0.3387(6)	0.8726(3)	0.0173(6)
H9	0.556937	0.398759	0.894875	0.021*
C10	0.62434(10)	0.4612(6)	0.8936(3)	0.0170(6)
H10	0.624690	0.606480	0.930955	0.020*
C11	0.66434(11)	0.3752(5)	0.8607(3)	0.0157(6)
C12	0.66356(11)	0.1620(6)	0.8063(3)	0.0163(6)
H12	0.690670	0.101474	0.783930	0.020*
C13	0.62348(10)	0.0368(6)	0.7844(3)	0.0167(6)
H13	0.622936	−0.108207	0.746686	0.020*
C14	0.70685(11)	0.5178(6)	0.8814(3)	0.0193(7)

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Abstract

$C_{14}H_{12}Br_2O$, monoclinic, $C2$ (no. 5), $a = 29.7356(3)$ Å, $b = 5.88712(4)$ Å, $c = 11.10915(9)$ Å, $\beta = 99.1700(8)^\circ$, $V = 1919.88(3)$ Å³, $Z = 6$, $R_{\text{gt}}(F) = 0.0166$, $wR_{\text{ref}}(F^2) = 0.0443$, $T = 100(2)$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Di(4-bromobenzyl)tin dibromide was synthesised by the direct reaction of 4-bromobenzyl bromide (Merck) and

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H14A	0.702225	0.655973	0.830156	0.023*
H14B	0.713253	0.565810	0.967851	0.023*
C15	0.78371(10)	0.5299(6)	0.8572(3)	0.0195(7)
H15A	0.790202	0.607906	0.937059	0.023*
H15B	0.778801	0.647046	0.792493	0.023*
C16	0.82363(10)	0.3810(5)	0.8398(3)	0.0155(7)
C17	0.81764(11)	0.1725(6)	0.7811(3)	0.0172(6)
H17	0.787784	0.121274	0.749548	0.021*
C18	0.85501(10)	0.0381(6)	0.7680(3)	0.0177(6)
H18	0.850948	−0.105026	0.728238	0.021*
C19	0.89837(10)	0.1166(6)	0.8141(3)	0.0170(7)
C20	0.90519(10)	0.3266(6)	0.8701(3)	0.0178(6)
H20	0.935093	0.380005	0.899128	0.021*
C21	0.86749(10)	0.4572(6)	0.8828(3)	0.0180(6)
H21	0.871680	0.601102	0.921646	0.022*

metallic tin powder (Merck) in toluene according to a literature procedure [5]. The prepared organotin compound was recrystallized in dimethyl sulfoxide together with few drops of water. The title compound was obtained as side-product from the recrystallisation process.

Yield: 0.05 g (14.0%). **M.pt** (Mel-temp II digital melting point apparatus): 450–452 K. **IR** (Bruker Vertex 70v FTIR Spectrophotometer; cm^{−1}): 1470 (m) ν(CC), 1034 (m) ν(CO). **¹H NMR** (Bruker Ascend 400 MHz NMR spectrometer, chemical shifts relative to Me₄Si, DMSO-*d*₆ solution; ppm): 3.38 (s, 4H, CH₂), 7.11–7.28 (m, 4H, Ph-H), 7.33–7.50 (m, 4H, Ph-H). **¹³C{¹H} NMR** (as for ¹H NMR): 40.6 (CH₂), 127.1, 127.8, 129.9, 130.3 (Ph-C).

Experimental details

The hydrogen atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with *U*_{iso}(H) = 1.2*U*_{eq}(C). The absolute structure was determined based on differences in Friedel pairs included in the data set (Flack-Parsons parameter: 0.000(12) using 1382 quotients). The maximum and minimum residual electron density peaks of 0.62 and 0.25 e Å^{−3}, respectively, were located 0.95 and 0.61 Å from the H7b and Br1 atoms, respectively.

Comment

For a rather simple composition, crystal structure determinations of dibenzylether molecules with the general formula ArCH₂OCH₂Ar are comparatively rare. The structure of the parent compound, PhCH₂OCH₂Ph is known [6], as are symmetric 2,2'-Br₂ [7], 2,2'-I₂ [8], 3,3'-(NO₂)₂ [9], 4,4'-(CN)₂ [10] and 3,4,3',4'-(OMe)₄ [11] derivatives. Herein, the crystal and molecular structures of 4-BrPhCH₂OCH₂PhBr-4 (I) are described.

Compound (I) became available as a side-product as detailed in the "Source of material".

The crystallographic asymmetric unit of (I) comprises one-half molecule, being disposed about a 2-fold axis with the O atom lying on the axis, and a full molecule in a general position. The molecular structures in (I) are shown in the figure (70% displacement ellipsoids; unlabelled atoms for the Br1-containing molecule are related by the symmetry operation 1 − *x*, *y*, 1 − *z*). The molecules, in common with the literature precedents, feature a central O atom connected on either side by benzyl/substituted benzyl substituents. However, non-trivial conformational differences are apparent, specifically in the relative disposition of the aryl substituents. For the 2-fold symmetric molecule in (I), the dihedral angle between the aryl rings is 48.94(9)°, which compares to 15.96(10)° for the non-symmetric molecule. The other obvious difference between the molecules relates to the C_{ring}–C_{methylene}–O–C_{methylene} torsion angles which are 2 × 164.7(3)° for the Br1-molecules, and 173.3(3) and 173.4(3) Å for the Br2-molecule. The aforementioned parameters lie within the ranges of comparable values in the literature structures. Thus, the dihedral angle between rings in the 2,2'-Br₂ [7] derivative is a small 3.1° and the widest dihedral angle of 57.38(7)° is found in the 4,4'-(CN)₂ [10] derivative. The greatest difference in the C_{ring}–C_{methylene}–O–C_{methylene} torsion angles, indicating the largest twist in the central residue is found in the 3,4,3',4'-(OMe)₄ [11] species, i.e. 73.27(18) and 177.42(14)°. In all of the other structures, the differences in these torsion angles is less than 10°.

In the crystal of (I), weak non-covalent π···π stacking [Cg(C1–C6)···Cg(C16–C21)]ⁱ = 3.8582(19) Å, angle of inclination = 1.51(16)° for symmetry operation (i) 3/2 − *x*, 1/2 + *y*, 1 − *z*] and four independent phenyl-C–H···π(phenyl) [shortest contact: C13–H13···Cg(C1–C6)]ⁱⁱ = 2.73 Å with angle at H13 = 132° for (ii) *x*, −1 + *y*, *z*] combine to assemble molecules into a three-dimensional architecture.

A further analysis of the molecular packing scheme was conducted by calculating the Hirshfeld surfaces and two-dimensional fingerprint plots (overall and decomposed) employing Crystal Explorer 17 [12] using standard protocols [13]. First and foremost, the calculations indicated distinct percentage contributions for the two independent molecules comprising the asymmetric unit [13]. As anticipated from the description of the molecular packing, significant contributions to the surface contacts revealed the dominance of H···H = 31.6% [31.9% for the Br2-molecule] and C···H/H···C = 21.3% [27.1%]. Very significant contributions are also made by Br···H/H···Br contacts, i.e. 35.6 and 31.7%, respectively, but at separations longer than the sum of the van der Waals radii. The same is true of Br···Br contacts [2.9 and 2.6%]. Other notable contacts are Br···C/C···Br

[1.6 and 0.8%], Br \cdots O/O \cdots Br [1.1 and 0.5%], O \cdots H/H \cdots O [0.6 and 2.6%] and C \cdots C [5.4 and 2.7%].

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