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Dimethyl 5,5'-methylenebis(2-hydroxybenzoate)

Samuel Guieu,^{a*} Paula Brandão,^b João Rocha^b and Artur M. S. Silva^a^aUniversity of Aveiro, QOPNA, Department of Chemistry, 3810-193 Aveiro, Portugal, and ^bUniversity of Aveiro, CICECO, Department of Chemistry, 3810-193 Aveiro, Portugal

Correspondence e-mail: sguieu@ua.pt

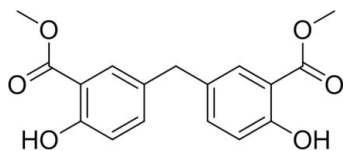
Received 27 March 2012; accepted 11 April 2012

Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.040; wR factor = 0.113; data-to-parameter ratio = 16.1.

In the title compound, $\text{C}_{17}\text{H}_{16}\text{O}_6$, the two methyl salicylate moieties are related by crystallographic twofold rotational symmetry with the two benzene rings close to being perpendicular [inter-ring dihedral angle = $86.6(8)^\circ$]. Intramolecular phenolic $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds with carboxyl O-atom acceptors are present, with these groups also involved in centrosymmetric cyclic intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonding associations [graph set $R_2^2(4)$], giving infinite chains extending across (101).

Related literature

For the chemistry and applications of methylene bisphenol derivatives, see: Ogata *et al.* (1975); Méric *et al.* (1993); Shrestha *et al.* (2007); Cameron *et al.* (2002). For the preparation, see: Cushman & Kanamathareddy (1990); Méric *et al.* (1993). For the structures of similar compounds, see: Lu *et al.* (2011); Zhang *et al.* (2009); Liu *et al.* (2009). For graph-set analysis, see Etter *et al.* (1990). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$\text{C}_{17}\text{H}_{16}\text{O}_6$
 $M_r = 316.31$
 Monoclinic, $C2/c$
 $a = 20.4168(13)$ Å
 $b = 4.9300(3)$ Å

$c = 15.5470(12)$ Å
 $\beta = 111.290(3)^\circ$
 $V = 1458.08(17)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation

$\mu = 0.11$ mm⁻¹
 $T = 150$ K

0.38 × 0.30 × 0.24 mm

Data collection

Bruker SMART CCD-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2008)
 $T_{\min} = 0.953$, $T_{\max} = 0.970$

8440 measured reflections
 1756 independent reflections
 1568 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.113$
 $S = 0.96$
 1756 reflections
 109 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.23$ e Å⁻³
 $\Delta\rho_{\min} = -0.33$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1}\cdots\text{O2}$	0.87 (2)	1.87 (2)	2.6457 (12)	147 (2)
$\text{O1}-\text{H1}\cdots\text{O2}^i$	0.87 (2)	2.32 (1)	3.0067 (11)	134 (9)

Symmetry code: (i) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 2$.

Data collection: SMART (Bruker, 2008); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZS2198).

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supporting information

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Dimethyl 5,5'-methylenebis(2-hydroxybenzoate)

Samuel Guieu, Paula Brandão, João Rocha and Artur M. S. Silva

S1. Comment

The title compound $C_{17}H_{16}O_6$ was first reported as a building block for polymer synthesis (Ogata *et al.*, 1975). It is a useful precursor for organic polymers, metal-organic frameworks, cage compounds (Méric *et al.*, 1993) and biologically active compounds (Shrestha *et al.*, 2007; Cameron *et al.*, 2002). In the title compound (Fig. 1), the two methyl salicylate moieties are related by crystallographic twofold rotational symmetry with the two phenyl rings close to perpendicular [inter-ring dihedral angle = $86.6(8)^\circ$]. Bond lengths and angles are within normal ranges (Allen *et al.*, 1987).

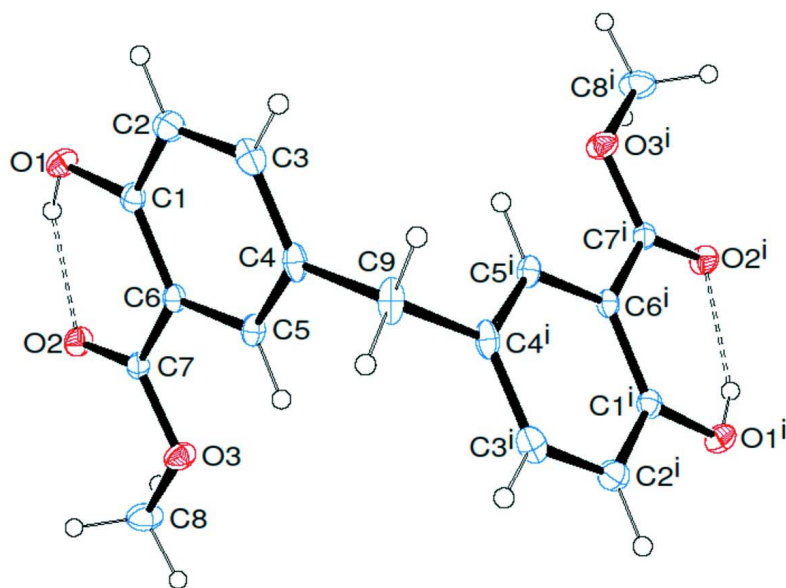
Intramolecular phenolic O—H \cdots O hydrogen bonds with carboxyl O-atom acceptors are present, with these groups also involved in centrosymmetric cyclic intermolecular hydrogen-bonding associations [graph set $R^2_2(4)$ (Etter *et al.*, 1990)], making the ester group essentially coplanar with the phenyl ring [torsion angle C1—C6—C7—O3, $178.64(9)^\circ$]. The molecules are involved in centrosymmetric cyclic intermolecular phenolic O—H \cdots O_{carboxyl} hydrogen-bonding associations [graph set $R^2_2(4)$ giving infinite chains extending across (101) (Figs. 2, 3).

S2. Experimental

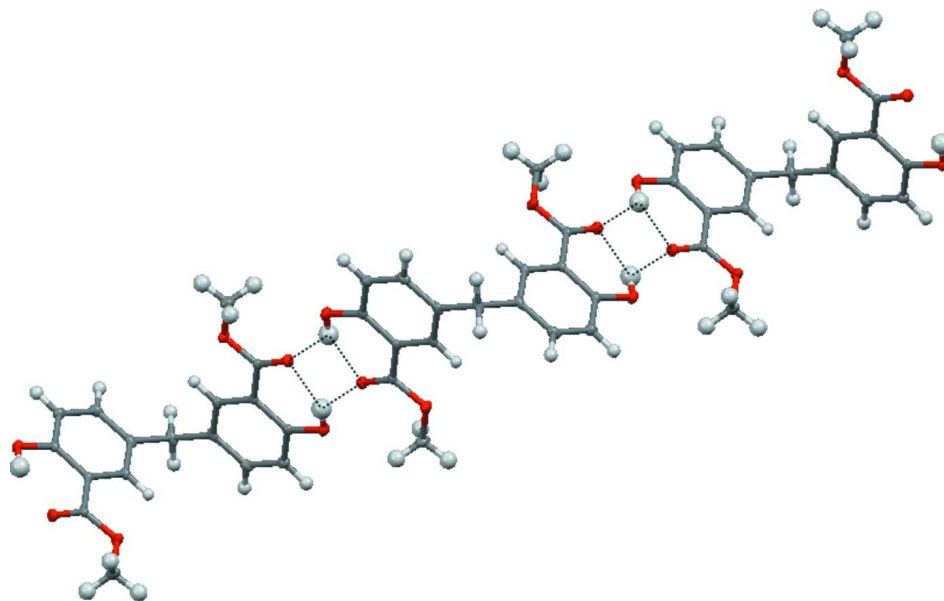
The title compound was prepared in two steps starting with salicylic acid. 5,5'-Methylenebis(salicylic acid) was prepared according to a known procedure (Cushman *et al.*, 1990), and was then esterified with methanol and a catalytic amount of sulfuric acid (Méric *et al.*, 1993). Slow evaporation of a saturated solution in dichloromethane gave single crystals suitable for X-ray diffraction.

S3. Refinement

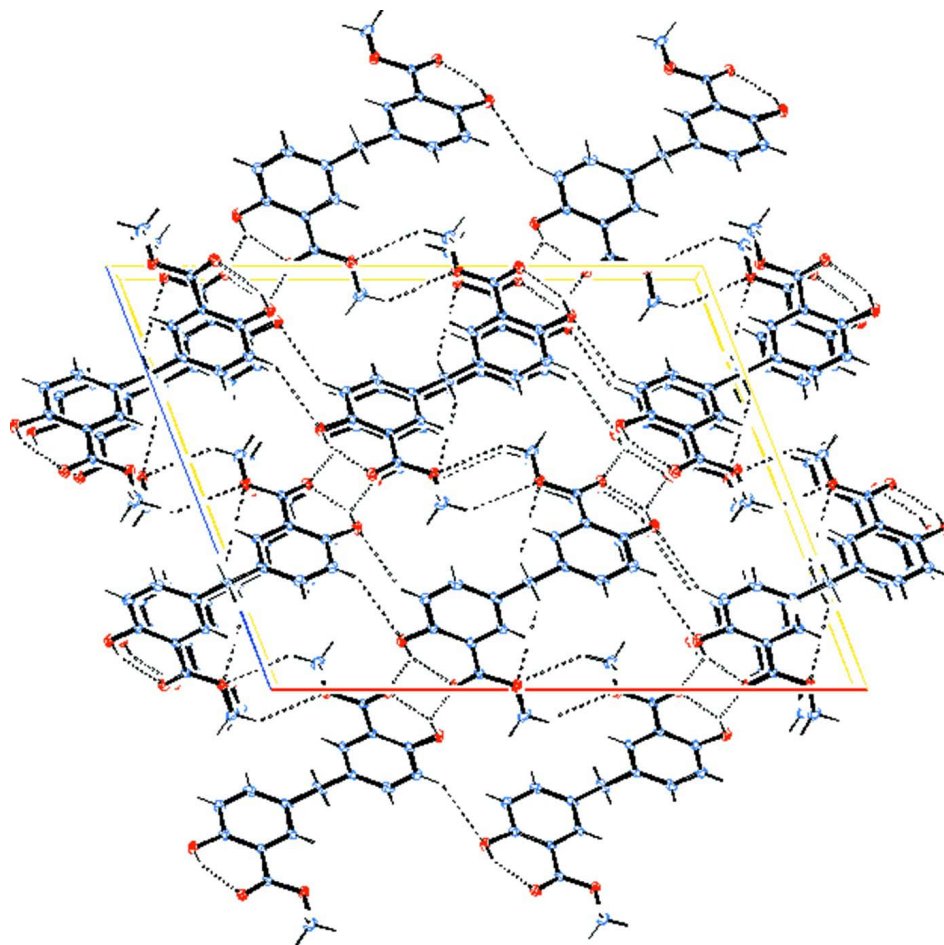
The phenolic H-atom (H1) was located in a difference Fourier map and both positional and isotropic displacement parameters were refined. All other H-atoms were placed in geometrically idealized positions and refined using a riding model with C—H = 0.95 Å (aromatic), 0.98 Å (methylene) or 0.97 Å (methyl) and $U_{iso}(H) = 1.2U_{eq}(C)$ (aromatic or methylene) or $U_{iso}(H) = 1.5U_{eq}(C)$ (methyl).

**Figure 1**

The molecular structure of the title compound showing atom numbering and displacement ellipsoids drawn at the 30% probability level. The intramolecular hydrogen bonds are shown as dashed lines. Symmetry code: (i) $-x + 1, y, -z + 1/2$.

**Figure 2**

The one-dimensional hydrogen-bonded chains in the title compound, with hydrogen bonds shown as dashed lines. Displacement ellipsoids are drawn at the 30% probability level.

**Figure 3**

The packing of the title compound in the unit cell viewed down the *b* axis, with hydrogen bonds and other intermolecular interactions shown as dashed lines.

Dimethyl 5,5'-methylenebis(2-hydroxybenzoate)

Crystal data

$C_{17}H_{16}O_6$

$M_r = 316.31$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 20.4168$ (13) Å

$b = 4.9300$ (3) Å

$c = 15.5470$ (12) Å

$\beta = 111.290$ (3)°

$V = 1458.08$ (17) Å³

$Z = 4$

$F(000) = 664$

$D_x = 1.441$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 8440 reflections

$\theta = 2.8$ – 27.9 °

$\mu = 0.11$ mm⁻¹

$T = 150$ K

Block, colourless

$0.38 \times 0.30 \times 0.24$ mm

Data collection

Bruker SMART CCD-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω and ϕ scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2008)

$T_{\min} = 0.953$, $T_{\max} = 0.970$

8440 measured reflections
 1756 independent reflections
 1568 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

$\theta_{\text{max}} = 27.9^\circ$, $\theta_{\text{min}} = 4.1^\circ$
 $h = -26 \rightarrow 21$
 $k = -6 \rightarrow 6$
 $l = -19 \rightarrow 20$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.113$
 $S = 0.96$
 1756 reflections
 109 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0724P)^2 + 0.9516P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.049$
 $\Delta\rho_{\text{max}} = 0.23 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.33 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
H1	0.2434 (10)	1.009 (5)	0.9251 (15)	0.070 (6)*	
O2	0.18996 (4)	1.12860 (16)	0.99304 (5)	0.0260 (2)	
O1	0.24736 (4)	0.89366 (17)	0.88455 (6)	0.0265 (2)	
O3	0.08604 (4)	0.98089 (17)	0.99095 (6)	0.0284 (2)	
C5	0.07384 (5)	0.6081 (2)	0.85532 (7)	0.0212 (2)	
H5	0.0372	0.6288	0.8789	0.025*	
C6	0.13366 (5)	0.7717 (2)	0.89054 (7)	0.0189 (2)	
C2	0.18118 (6)	0.5483 (2)	0.78810 (8)	0.0269 (3)	
H2	0.2178	0.5240	0.7648	0.032*	
C7	0.14042 (5)	0.9762 (2)	0.96221 (7)	0.0196 (2)	
C3	0.12105 (6)	0.3904 (2)	0.75449 (8)	0.0277 (3)	
H3	0.1170	0.2602	0.7078	0.033*	
C1	0.18813 (5)	0.7425 (2)	0.85599 (7)	0.0212 (2)	
C4	0.06631 (5)	0.4174 (2)	0.78730 (7)	0.0238 (2)	
C9	0.0000	0.2479 (3)	0.7500	0.0296 (4)	
H9A	-0.0029	0.1295	0.7999	0.036*	0.50
H9B	0.0029	0.1295	0.7001	0.036*	0.50
C8	0.09263 (7)	1.1785 (3)	1.06230 (9)	0.0350 (3)	
H8A	0.0510	1.1700	1.0796	0.053*	
H8B	0.0966	1.3604	1.0393	0.053*	

H8C 0.1347 1.1389 1.1165 0.053*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0226 (4)	0.0255 (4)	0.0290 (4)	-0.0081 (3)	0.0084 (3)	-0.0051 (3)
O1	0.0221 (4)	0.0265 (4)	0.0335 (5)	-0.0035 (3)	0.0132 (3)	-0.0013 (3)
O3	0.0247 (4)	0.0324 (5)	0.0315 (4)	-0.0085 (3)	0.0142 (3)	-0.0101 (3)
C5	0.0180 (4)	0.0180 (5)	0.0235 (5)	0.0006 (4)	0.0027 (4)	0.0024 (4)
C6	0.0178 (4)	0.0171 (5)	0.0188 (5)	0.0007 (3)	0.0031 (4)	0.0023 (4)
C2	0.0289 (5)	0.0259 (5)	0.0266 (5)	0.0049 (4)	0.0110 (4)	0.0009 (4)
C7	0.0175 (4)	0.0200 (5)	0.0191 (5)	-0.0013 (3)	0.0043 (4)	0.0025 (4)
C3	0.0335 (6)	0.0207 (5)	0.0235 (5)	0.0050 (4)	0.0039 (4)	-0.0024 (4)
C1	0.0200 (5)	0.0199 (5)	0.0218 (5)	0.0014 (4)	0.0052 (4)	0.0045 (4)
C4	0.0227 (5)	0.0157 (5)	0.0242 (5)	0.0020 (4)	-0.0021 (4)	0.0026 (4)
C9	0.0247 (7)	0.0162 (7)	0.0350 (8)	0.000	-0.0045 (6)	0.000
C8	0.0396 (7)	0.0382 (7)	0.0338 (6)	-0.0085 (5)	0.0211 (5)	-0.0124 (5)

Geometric parameters (Å, °)

O2—C7	1.2104 (13)	C2—C1	1.3938 (15)
O1—C1	1.3508 (13)	C2—H2	0.9500
O1—H1	0.87 (2)	C3—C4	1.3932 (17)
O3—C7	1.3390 (12)	C3—H3	0.9500
O3—C8	1.4455 (14)	C4—C9	1.5157 (13)
C5—C4	1.3811 (15)	C9—C4 ⁱ	1.5157 (13)
C5—C6	1.3989 (14)	C9—H9A	0.9900
C5—H5	0.9500	C9—H9B	0.9900
C6—C1	1.4071 (14)	C8—H8A	0.9800
C6—C7	1.4715 (14)	C8—H8B	0.9800
C2—C3	1.3857 (16)	C8—H8C	0.9800
C1—O1—H1	106.9 (13)	O1—C1—C6	123.74 (10)
C7—O3—C8	114.23 (8)	C2—C1—C6	118.82 (10)
C4—C5—C6	122.07 (10)	C5—C4—C3	117.65 (10)
C4—C5—H5	119.0	C5—C4—C9	120.26 (10)
C6—C5—H5	119.0	C3—C4—C9	122.08 (9)
C5—C6—C1	119.36 (9)	C4—C9—C4 ⁱ	113.07 (12)
C5—C6—C7	121.34 (9)	C4—C9—H9A	109.0
C1—C6—C7	119.30 (9)	C4 ⁱ —C9—H9A	109.0
C3—C2—C1	120.27 (10)	C4—C9—H9B	109.0
C3—C2—H2	119.9	C4 ⁱ —C9—H9B	109.0
C1—C2—H2	119.9	H9A—C9—H9B	107.8
O2—C7—O3	122.15 (9)	O3—C8—H8A	109.5
O2—C7—C6	124.07 (9)	O3—C8—H8B	109.5
O3—C7—C6	113.78 (8)	H8A—C8—H8B	109.5
C2—C3—C4	121.81 (10)	O3—C8—H8C	109.5
C2—C3—H3	119.1	H8A—C8—H8C	109.5

C4—C3—H3	119.1	H8B—C8—H8C	109.5
O1—C1—C2	117.44 (9)		
C8—O3—C7—O2	-1.07 (15)	C3—C4—C5—C6	0.43 (15)
C8—O3—C7—C6	179.17 (9)	C9—C4—C5—C6	-178.93 (9)
O1—C1—C2—C3	-178.69 (10)	C3—C4—C9—C4 ⁱ	-123.32 (10)
C6—C1—C2—C3	1.01 (16)	C5—C4—C9—C4 ⁱ	56.01 (11)
O1—C1—C6—C5	178.95 (10)	C4—C5—C6—C1	0.00 (16)
O1—C1—C6—C7	-0.29 (15)	C4—C5—C6—C7	179.24 (10)
C2—C1—C6—C5	-0.73 (15)	C1—C6—C7—O2	1.60 (16)
C2—C1—C6—C7	-179.97 (10)	C1—C6—C7—O3	-178.64 (9)
C1—C2—C3—C4	-0.58 (17)	C5—C6—C7—O2	-177.63 (10)
C2—C3—C4—C5	-0.15 (16)	C5—C6—C7—O3	2.13 (14)
C2—C3—C4—C9	179.20 (10)		

Symmetry code: (i) $-x, y, -z+3/2$.

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O1—H1...O2	0.87 (2)	1.87 (2)	2.6457 (12)	147 (2)
O1—H1...O2 ⁱⁱ	0.87 (2)	2.32 (1)	3.0067 (11)	134 (9)

Symmetry code: (ii) $-x+1/2, -y+5/2, -z+2$.