



# Crystal structure of dimethyl 4,4'-dimethoxybiphenyl-3,3'-dicarboxylate

Fredrik Lundvall,<sup>a\*</sup> Pascal D. C. Dietzel<sup>b</sup> and Helmer Fjellvåg<sup>a</sup><sup>a</sup>Centre for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, PO Box 1126, 0315 Oslo, Norway, and <sup>b</sup>Department of Chemistry, University of Bergen, PO Box 7803, 5020 Bergen, Norway.

\*Correspondence e-mail: fredrik.lundvall@smn.uio.no

Received 30 January 2016

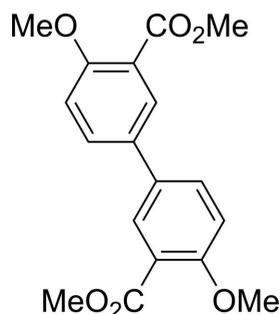
Accepted 9 February 2016

Edited by M. Weil, Vienna University of  
Technology, Austria**Keywords:** crystal structure; intermediate  
compound for organic linkers in MOF synthesis;  
centrosymmetric molecule.**CCDC reference:** 1452330**Supporting information:** this article has  
supporting information at journals.iucr.org/e

In the title compound,  $C_{18}H_{18}O_6$ , the benzene rings are coplanar due to the centrosymmetric nature of the molecule, with an inversion centre located at the midpoint of the C—C bond between the two rings. Consequently, the methyl carboxylate substituents are oriented in a *trans* fashion with regards to the bond between the benzene rings. The methyl carboxylate and methoxy substituents are rotated slightly out of plane relative to their parent benzene rings, with dihedral and torsion angles of 18.52 (8) and  $-5.22$  (15)°, respectively. The shortest O···H contact between neighbouring molecules is about 2.5 Å. Although some structure-directing contributions from C—H···O hydrogen-bonding interactions are possible, the crystal packing seems primarily directed by weak van der Waals forces.

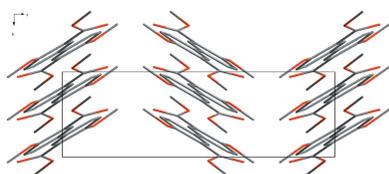
## 1. Chemical context

The title compound is an intermediate in the synthesis of 4,4'-dimethoxybiphenyl-3,3'-biphenyldicarboxylic acid, an organic linker for use in the synthesis of coordination polymers (Lundvall *et al.*, 2016). The title compound,  $C_{18}H_{18}O_6$ , has previously been reported (Wang *et al.*, 2009; Kar *et al.*, 2009), however, its crystal structure was undetermined up until now.



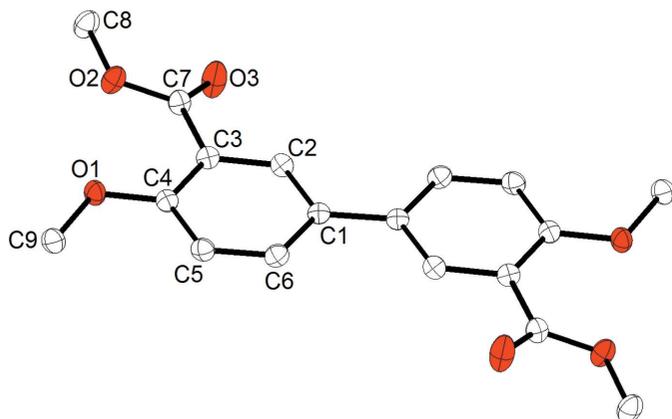
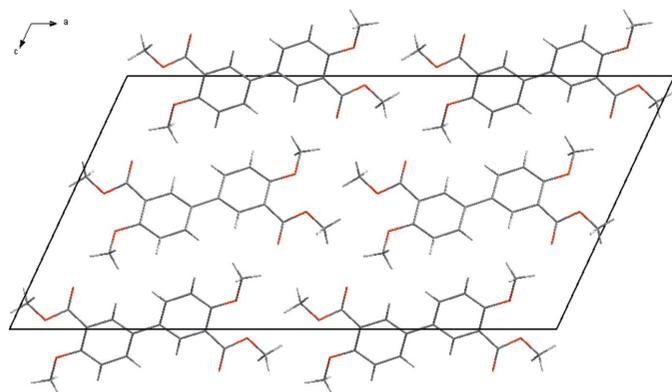
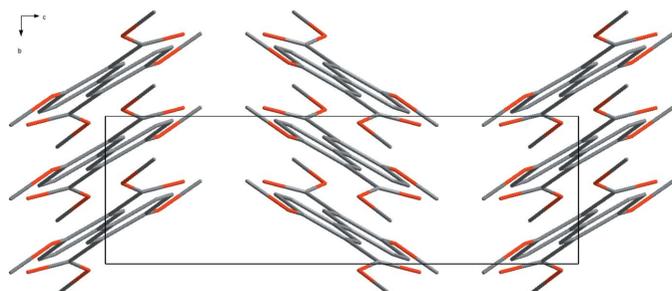
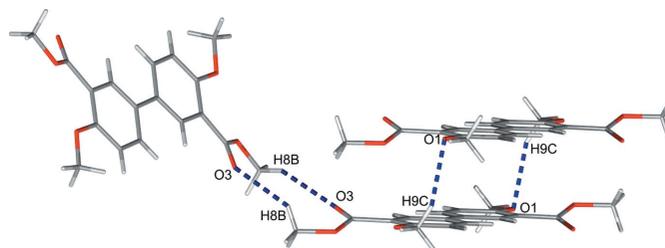
## 2. Structural commentary

The asymmetric unit of the title compound comprises one half of the molecule, with an inversion centre located at the midpoint of the benzene–benzene bond (Fig. 1). The benzene rings are coplanar due to symmetry. This is somewhat unexpected since a slight torsion between the two rings is a common feature in biphenyl compounds. The methyl carboxylate substituents are oriented *trans* relative to the benzene–benzene bond, and the plane of the substituent makes a dihedral angle of 18.52 (8)° relative to the parent benzene ring. The methoxy substituent is nearly coplanar with the parent benzene ring, and a torsion angle



**Table 1**  
 Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C9-H9C\cdots O1^i$	0.98	2.55	3.4759 (15)	158
$C8-H8B\cdots O3^{ii}$	0.98	2.50	3.3407 (15)	144

 Symmetry codes: (i)  $x, y-1, z$ ; (ii)  $-x, y, -z-\frac{1}{2}$ .

**Figure 1**  
 The molecular structure of the title compound with atom labels and 50% probability displacement ellipsoids. Non-labelled atoms are generated by the symmetry code  $(-x + \frac{1}{2}, -y + \frac{1}{2}, -z)$ . H atoms have been omitted for clarity.

**Figure 2**  
 Packing diagram of the title compound viewed along the  $b$  axis.

**Figure 3**  
 Packing diagram of the title compound viewed along the  $a$  axis. H atoms have been omitted for clarity.

**Figure 4**  
 Graphical representation of the shortest intermolecular  $O\cdots H$  contacts, illustrated as dashed blue lines.

$C5-C4-O1-C9$  of only  $-5.22(15)^\circ$  is observed. The methyl groups of the methyl carboxylate and methoxy substituents are oriented away from each other to accommodate the steric demands of these groups.

### 3. Supramolecular features

The molecules are packed in the unit cell with the axis of the biphenyl scaffolds parallel to each other. The axis of the biphenyl moiety is oriented approximately  $20^\circ$  off the  $a$  axis of the unit cell (Fig. 2), and the molecules form corrugated layers extending parallel to the  $ac$  plane (Fig. 3). The packing is not directed by strong intermolecular bonding since the shortest  $O\cdots H$  contact is about  $2.5 \text{ \AA}$  (Table 1). However, weak  $C-H\cdots O$  interactions between neighbouring molecules seem to have an influence on the crystal packing (Fig. 4).

**Table 2**  
 Experimental details.

Crystal data	
Chemical formula	$C_{18}H_{18}O_6$
$M_r$	330.32
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	105
$a, b, c$ (Å)	28.5800 (14), 4.0632 (2), 14.4806 (7)
$\beta$ (°)	115.100 (1)
$V$ (Å <sup>3</sup> )	1522.78 (13)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.11
Crystal size (mm)	0.56 × 0.29 × 0.22
Data collection	
Diffractometer	Bruker PHOTON CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2007)
$T_{\min}, T_{\max}$	0.602, 0.746
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	17902, 2053, 1819
$R_{\text{int}}$	0.037
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.685
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.038, 0.109, 1.10
No. of reflections	2053
No. of parameters	111
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.41, -0.24

Computer programs: APEX2 and SAINT (Bruker, 2007), SHELXS97 (Sheldrick, 2008), SHELXL2014 (Sheldrick, 2015), WinGX (Farrugia, 2012), DIAMOND (Brandenburg, 2004), ChemBioDraw (Cambridge Soft, 2009) and publCIF (Westrip, 2010).

### 4. Synthesis and crystallization

The title compound was synthesized by a slightly modified procedure of the method described by Wang *et al.* (2009). Synthetic details are given in the Supporting Information of our recent contribution (Lundvall *et al.*, 2016). Single crystals suitable for structure determination were obtained by recrystallizing the title compound from chloroform solution.

### 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were positioned geometrically at distances of 0.95 (CH) and 0.98 Å (CH<sub>3</sub>) and were refined using a riding model with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{CH})$  and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{CH}_3)$ .

### Acknowledgements

We acknowledge support from the Research Council of Norway (Project No. 190980), the Norwegian national infra-

structure for X-ray diffraction and scattering (RECX) and the Department of Chemistry, UiO.

### References

- Brandenburg, K. (2004). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Bruker (2007). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cambridge Soft (2009). *ChemBioDraw Ultra*. Cambridge Soft Corporation, Cambridge, Massachusetts, USA.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Kar, A., Mangu, N., Kaiser, H. M. & Tse, M. K. (2009). *J. Organomet. Chem.* **694**, 524–537.
- Lundvall, F., Vajeeston, P., Wragg, D. S., Dietzel, P. D. C. & Fjellvåg, H. (2016). *Cryst. Growth Des.* **16**, 339–346.
- Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst. C* **71**, 3–8.
- Wang, L., Xiao, Z.-Y., Hou, J.-L., Wang, G.-T., Jiang, X.-K. & Li, Z. (2009). *Tetrahedron*, **65**, 10544–10551.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

## supporting information

*Acta Cryst.* (2016). E72, 328-330 [doi:10.1107/S2056989016002449]

## Crystal structure of dimethyl 4,4'-dimethoxybiphenyl-3,3'-dicarboxylate

Fredrik Lundvall, Pascal D. C. Dietzel and Helmer Fjellvåg

## Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015) and *WinGX* (Farrugia, 2012); molecular graphics: *DIAMOND* (Brandenburg, 2004) and *ChemBioDraw* (Cambridge Soft, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

## Dimethyl 4,4'-dimethoxybiphenyl-3,3'-dicarboxylate

## Crystal data

$C_{18}H_{18}O_6$	$F(000) = 696$
$M_r = 330.32$	$D_x = 1.441 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 28.5800 (14) \text{ \AA}$	Cell parameters from 9942 reflections
$b = 4.0632 (2) \text{ \AA}$	$\theta = 2.8\text{--}29.1^\circ$
$c = 14.4806 (7) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$\beta = 115.100 (1)^\circ$	$T = 105 \text{ K}$
$V = 1522.78 (13) \text{ \AA}^3$	Needle, colourless
$Z = 4$	$0.56 \times 0.29 \times 0.22 \text{ mm}$

## Data collection

Bruker PHOTON CCD diffractometer	17902 measured reflections
Radiation source: fine-focus sealed tube	2053 independent reflections
Graphite monochromator	1819 reflections with $I > 2\sigma(I)$
$\omega$ scans	$R_{\text{int}} = 0.037$
Absorption correction: multi-scan ( <i>SADABS</i> ; Bruker, 2007)	$\theta_{\text{max}} = 29.2^\circ$ , $\theta_{\text{min}} = 2.8^\circ$
$T_{\text{min}} = 0.602$ , $T_{\text{max}} = 0.746$	$h = -38 \rightarrow 38$
	$k = -5 \rightarrow 5$
	$l = -19 \rightarrow 19$

## Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.038$	H-atom parameters constrained
$wR(F^2) = 0.109$	$w = 1/[\sigma^2(F_o^2) + (0.0534P)^2 + 1.1903P]$
$S = 1.10$	where $P = (F_o^2 + 2F_c^2)/3$
2053 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
111 parameters	$\Delta\rho_{\text{max}} = 0.41 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

*Special details*

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

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.22923 (4)	0.2306 (3)	0.01755 (7)	0.0163 (2)
C2	0.17986 (4)	0.3583 (3)	-0.03782 (7)	0.0175 (2)
H2	0.1730	0.4703	-0.0998	0.021*
C3	0.14011 (4)	0.3300 (3)	-0.00694 (7)	0.0170 (2)
C4	0.14924 (4)	0.1625 (3)	0.08424 (8)	0.0170 (2)
C5	0.19832 (4)	0.0299 (3)	0.14041 (8)	0.0193 (2)
H5	0.2052	-0.0851	0.2020	0.023*
C6	0.23708 (4)	0.0637 (3)	0.10753 (8)	0.0193 (2)
H6	0.2701	-0.0293	0.1473	0.023*
C7	0.09039 (4)	0.4858 (3)	-0.07720 (8)	0.0192 (2)
C8	0.01027 (4)	0.7077 (3)	-0.10223 (9)	0.0256 (3)
H8A	-0.0111	0.7454	-0.0653	0.038*
H8B	-0.0086	0.5685	-0.1618	0.038*
H8C	0.0184	0.9191	-0.1246	0.038*
C9	0.11816 (5)	-0.0599 (3)	0.20034 (8)	0.0229 (2)
H9A	0.0868	-0.0586	0.2121	0.034*
H9B	0.1470	0.0309	0.2601	0.034*
H9C	0.1262	-0.2863	0.1888	0.034*
O1	0.10999 (3)	0.1361 (2)	0.11283 (6)	0.02064 (19)
O2	0.05778 (3)	0.5450 (2)	-0.03563 (6)	0.0232 (2)
O3	0.08127 (3)	0.5572 (3)	-0.16406 (7)	0.0354 (3)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0173 (5)	0.0161 (5)	0.0141 (4)	-0.0009 (4)	0.0053 (4)	-0.0023 (4)
C2	0.0182 (5)	0.0194 (5)	0.0133 (4)	-0.0012 (4)	0.0051 (4)	-0.0004 (4)
C3	0.0162 (4)	0.0181 (5)	0.0142 (4)	-0.0010 (4)	0.0040 (4)	-0.0018 (4)
C4	0.0187 (5)	0.0168 (5)	0.0156 (4)	-0.0020 (4)	0.0072 (4)	-0.0027 (4)
C5	0.0216 (5)	0.0201 (5)	0.0153 (4)	0.0013 (4)	0.0071 (4)	0.0023 (4)
C6	0.0186 (5)	0.0208 (5)	0.0164 (5)	0.0025 (4)	0.0054 (4)	0.0008 (4)
C7	0.0165 (5)	0.0223 (5)	0.0170 (5)	-0.0015 (4)	0.0055 (4)	0.0001 (4)
C8	0.0185 (5)	0.0324 (6)	0.0240 (5)	0.0064 (5)	0.0073 (4)	0.0036 (5)
C9	0.0288 (6)	0.0234 (6)	0.0203 (5)	0.0022 (4)	0.0141 (4)	0.0036 (4)
O1	0.0207 (4)	0.0247 (4)	0.0184 (4)	0.0013 (3)	0.0101 (3)	0.0038 (3)
O2	0.0193 (4)	0.0323 (5)	0.0172 (4)	0.0060 (3)	0.0068 (3)	0.0015 (3)
O3	0.0223 (4)	0.0622 (7)	0.0219 (4)	0.0115 (4)	0.0096 (3)	0.0158 (4)

## Geometric parameters (Å, °)

C1—C2	1.3940 (14)	C6—H6	0.9500
C1—C6	1.3998 (14)	C7—O3	1.2067 (14)
C1—C1 <sup>i</sup>	1.4846 (19)	C7—O2	1.3285 (13)
C2—C3	1.3909 (14)	C8—O2	1.4490 (13)
C2—H2	0.9500	C8—H8A	0.9800
C3—C4	1.4080 (14)	C8—H8B	0.9800
C3—C7	1.4928 (14)	C8—H8C	0.9800
C4—O1	1.3549 (12)	C9—O1	1.4293 (13)
C4—C5	1.3971 (15)	C9—H9A	0.9800
C5—C6	1.3859 (15)	C9—H9B	0.9800
C5—H5	0.9500	C9—H9C	0.9800
C2—C1—C6	116.04 (9)	O3—C7—O2	123.09 (10)
C2—C1—C1 <sup>i</sup>	121.65 (11)	O3—C7—C3	122.32 (10)
C6—C1—C1 <sup>i</sup>	122.31 (11)	O2—C7—C3	114.58 (9)
C3—C2—C1	123.36 (9)	O2—C8—H8A	109.5
C3—C2—H2	118.3	O2—C8—H8B	109.5
C1—C2—H2	118.3	H8A—C8—H8B	109.5
C2—C3—C4	119.32 (9)	O2—C8—H8C	109.5
C2—C3—C7	114.66 (9)	H8A—C8—H8C	109.5
C4—C3—C7	126.03 (9)	H8B—C8—H8C	109.5
O1—C4—C5	123.27 (9)	O1—C9—H9A	109.5
O1—C4—C3	118.48 (9)	O1—C9—H9B	109.5
C5—C4—C3	118.25 (10)	H9A—C9—H9B	109.5
C6—C5—C4	120.87 (10)	O1—C9—H9C	109.5
C6—C5—H5	119.6	H9A—C9—H9C	109.5
C4—C5—H5	119.6	H9B—C9—H9C	109.5
C5—C6—C1	122.15 (10)	C4—O1—C9	118.03 (8)
C5—C6—H6	118.9	C7—O2—C8	114.87 (9)
C1—C6—H6	118.9		
C6—C1—C2—C3	0.89 (16)	C2—C1—C6—C5	-0.64 (16)
C1 <sup>i</sup> —C1—C2—C3	-179.29 (11)	C1 <sup>i</sup> —C1—C6—C5	179.55 (12)
C1—C2—C3—C4	-0.55 (16)	C2—C3—C7—O3	17.33 (16)
C1—C2—C3—C7	179.71 (10)	C4—C3—C7—O3	-162.39 (12)
C2—C3—C4—O1	-179.68 (9)	C2—C3—C7—O2	-161.30 (10)
C7—C3—C4—O1	0.03 (16)	C4—C3—C7—O2	18.97 (16)
C2—C3—C4—C5	-0.08 (15)	C5—C4—O1—C9	-5.22 (15)
C7—C3—C4—C5	179.63 (10)	C3—C4—O1—C9	174.36 (10)
O1—C4—C5—C6	179.90 (10)	O3—C7—O2—C8	-0.89 (17)
C3—C4—C5—C6	0.32 (16)	C3—C7—O2—C8	177.74 (10)
C4—C5—C6—C1	0.05 (17)	C2—C1—C1 <sup>i</sup> —C6 <sup>i</sup>	0.2 (2)

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

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C9—H9C···O1 <sup>ii</sup>	0.98	2.55	3.4759 (15)	158
C8—H8B···O3 <sup>iii</sup>	0.98	2.50	3.3407 (15)	144

Symmetry codes: (ii)  $x, y-1, z$ ; (iii)  $-x, y, -z-1/2$ .