

2-Ethyl 3,4-dimethyl 4'-methylbiphenyl-
2,3,4-tricarboxylateSundari Bhaskaran,^a D.
Velmurugan,^{a*} K. Ravikumar,^b
A. K. Mohana Krishnan^c and
C. Prakash^c^aDepartment of Crystallography and Biophysics,
University of Madras, Guindy Campus, Chennai
600 025, India, ^bLaboratory of X-ray Crystal-
lography, Indian Institute of Chemical Tech-
nology, Hyderabad 500 007, India, and
^cDepartment of Organic Chemistry, University
of Madras, Guindy Campus, Chennai 600 025,
India

Correspondence e-mail: d_velu@yahoo.com

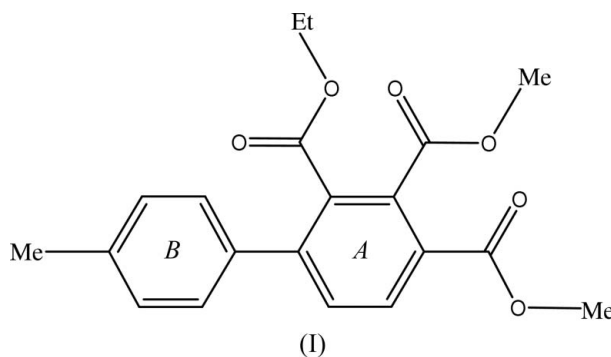
Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.074
 wR factor = 0.217
Data-to-parameter ratio = 18.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the title compound, $\text{C}_{20}\text{H}_{20}\text{O}_6$, the biphenyl twist angle is $48.2(1)^\circ$. All three ester groups are planar and they make dihedral angles of $63.6(1)$, $56.8(1)$ and $41.6(1)^\circ$ with the attached benzene ring. $\text{C}-\text{H}\cdots\text{O}$ interactions contribute to both molecular and crystal stability.

Comment

Compounds with an aromatic–aromatic bond, *i.e.* a single bond between aromatic rings such as phenyl rings, and their derivatives with extended structures (oligomers and polymers) have received considerable interest owing to their intriguing structural motifs and unique electroconductive, nonlinear optical and luminescence properties (Kovacic & Jones, 1987; Tour, 1996). The interest in the study of biphenyl derivatives concerns the search for hydrogen bonding and $\text{C}-\text{H}\cdots\text{O}$ interactions in aromatic compounds (Dobson & Gerkin, 1999c) and the influence of the hydrogen bonding substituents on such interactions. The structural analysis of the title compound, (I), was undertaken in order to look for hydrogen bonds, if any, and the $\text{C}-\text{H}\cdots\text{O}$ interactions that promote the stability.



The angles in benzene ring *A* range from $117.6(2)$ to $121.6(2)^\circ$ and in *B* from $117.4(2)$ to $121.8(3)^\circ$, deviating from 120° , a feature that is also observed in decachlorobiphenyl (Pedersen, 1975). All other distances and angles fall within normal limits (Table 1). In the ethyl ester, atom C15 deviates from the least-squares ester plane by $1.119(1)$ Å. The dihedral angle between the two rings comprising the biphenyl core, the biphenyl twist angle, is $48.2(1)^\circ$ (Fig. 1). The deviation from orthogonality can be attributed to the absence of a hydrogen-bonding substituent in the *ortho* position of the second benzene ring. For hydrogen-bonding substituents in the *ortho* position, the twist angles in the literature are $87.3(1)^\circ$ (Dobson & Gerkin, 1999a) and $87.5(2)^\circ$ (Dobson & Gerkin, 1999b). When there is no hydrogen-bonding substituent in the

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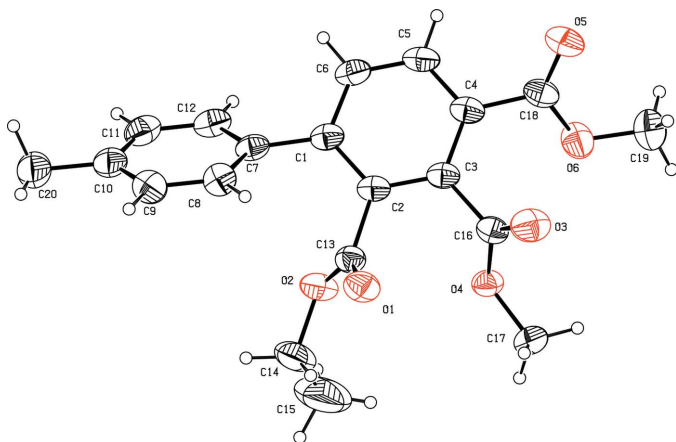


Figure 1
The molecular structure of the title compound showing 30% probability displacement ellipsoids.

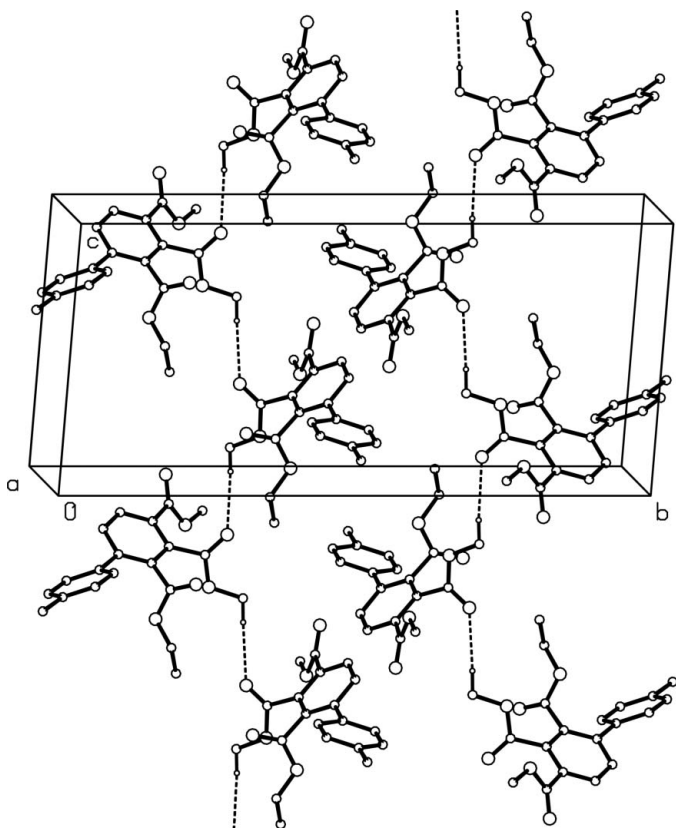


Figure 2
The molecular packing of (I), viewed approximately down the *a* axis. Hydrogen bonds are shown as dashed lines, and H atoms not involved in hydrogen bonding have been omitted.

ortho position, the twist angle [$36.3(1)^\circ$] deviates from orthogonality as evidenced by Sutherland & Rawas (1983). The twist angle of the present compound is comparable to that of the two polymorphic structures lacking an *ortho* substitution in the second ring (Subbiah Pandi, Velmurugan, Shanmuga Sundara Raj *et al.*, 2002; Subbiah Pandi, Velmurugan, Raghukumar *et al.*, 2002).

The non-H atoms of the ester groups each lie very nearly in a plane. The ester planes O1/C13/O2/C14/C15, O3/C16/O4/

C17 and O5/C18/O6/C19 are inclined at angles of $63.6(1)$, $56.8(1)$ and $41.6(1)^\circ$, respectively, to ring A. The two methyl ester planes are very nearly orthogonal [$89.1(1)$ and $89.0(1)^\circ$] to ring B and are oriented at an angle of $52.5(1)^\circ$ to each other. The ethyl ester plane makes a dihedral angle of $68.8(1)^\circ$ with ring B, $35.2(2)^\circ$ with the first methyl ester (C16/O3/O4/C17) and $82.2(1)^\circ$ with the second methyl ester (C18/O5/O6/C19).

In addition to van der Waals forces, the crystal packing is further stabilized by C—H···O hydrogen bonds. Atom C17 of the methoxycarbonyl group interacts with atom O3 at $(-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$, which generates a C—H···O interaction in a chain motif C(5) along the *c* axis (Fig. 2).

Experimental

A mixture of dimethylformamidedimethyl acetal (DMFDMA) (2.5 mmol) and β -phenylethyl crotonate (1 mmol) was refluxed for 4 h and then cooled to 333 K. DMAD (dimethyl acetylenedicarboxylate) (1.5 mmol) was added and the reaction was continued for another 30 min. The compound was recrystallized using an ethyl acetate and hexane mixture (1:1) to afford good quality crystals.

Crystal data

$C_{20}H_{20}O_6$
 $M_r = 356.36$
Monoclinic, $P2_1/n$
 $a = 6.7650(6) \text{ \AA}$
 $b = 23.8952(19) \text{ \AA}$
 $c = 12.0094(10) \text{ \AA}$
 $\beta = 105.670(1)^\circ$
 $V = 1869.2(3) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.266 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 3056 reflections
 $\theta = 2.4\text{--}27.9^\circ$
 $\mu = 0.09 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
Block, colourless
 $0.23 \times 0.21 \times 0.19 \text{ mm}$

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 ω scans
Absorption correction: none
21287 measured reflections
4398 independent reflections

3295 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$
 $\theta_{\text{max}} = 28.0^\circ$
 $h = -8 \rightarrow 8$
 $k = -31 \rightarrow 30$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.074$
 $wR(F^2) = 0.217$
 $S = 1.09$
4398 reflections
239 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1204P)^2 + 0.2698P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

O2—C13	1.316 (3)	O4—C17	1.451 (3)
O2—C14	1.459 (3)	O6—C18	1.320 (3)
O4—C16	1.320 (2)	O6—C19	1.452 (3)
C13—O2—C14	117.6 (2)	C10—C9—C8	121.8 (3)
C16—O4—C17	116.2 (2)	C11—C10—C9	117.6 (2)
C18—O6—C19	117.0 (2)	C10—C11—C12	121.5 (2)
C6—C1—C2	117.6 (2)	O1—C13—O2	125.6 (2)
C5—C6—C1	121.6 (2)	O3—C16—O4	125.1 (2)
C12—C7—C8	117.4 (2)	O5—C18—O6	123.7 (2)

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C17—H17B \cdots O3 ⁱ	0.96	2.52	3.473 (3)	171

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

The H atoms were positioned geometrically and were treated as riding on their parent C atoms, with C—H distances of 0.93–0.97 Å, and with $U_{\text{iso}}(\text{H})$ values of $1.5U_{\text{eq}}(\text{C})$ for methyl H and $1.2U_{\text{eq}}(\text{C})$ for other H atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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