Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

C—H···O interactions in diethyl 5,5′,6,6′-tetramethylbiphenyl-2,2′-dicarboxylate at 193 K

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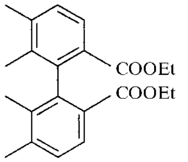
Received 16 March 2000
Accepted 8 May 2000

The title compound, $C_{22}H_{26}O_4$, crystallized in the centrosymmetric space group $P\bar{1}$ with one molecule as the asymmetric unit. Three leading intermolecular C—H···O interactions have H···O distances of 2.71, 2.73 (2) and 2.71 (2) Å and C—H···O angles of 167, 137.0 (15) and 163.1 (12)°. These interactions form ring and chain patterns. The biphenyl twist angle is 79.95 (6)°.

Comment

This report is one of a series on hydrogen bonding and C—H···O interactions in aromatic compounds. In this compound, conventional hydrogen bonds are of course absent, but significant C—H···O interactions were anticipated. The title compound, (I), crystallized in the centrosymmetric space group $P\bar{1}$ with one molecule as the asymmetric unit. The refined molecule and the labeling scheme are given in Fig. 1. Three leading intermolecular C—H···O interactions (Taylor & Kennard, 1982; Steiner & Desiraju, 1998) are present in this structure. The geometric parameters of these are given in Table 2. The results of basic first- and second-level graph-set analysis (Bernstein *et al.*, 1995) involving these interactions, labeled *a–c* for this purpose in the order of their appearance in Table 2, are given in Table 3. The three first-level rings occur about centers of symmetry; the second-level ring does not, consistent with the involvement of each interaction only once. Both chains propagate along [001]. These three interactions link a central molecule directly to only two neighboring molecules as shown in the stereodiagram, Fig. 2. It is of interest that, while atoms O2 and O4 are chemically equivalent, only O4 is involved in these leading interactions.



(I)

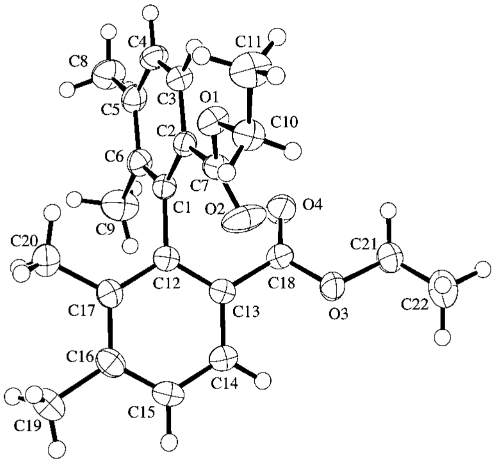


Figure 1
Compound (I), showing the labeling scheme, with displacement ellipsoids at the 50% level.

The phenyl rings are closely planar, the maximum deviation of a C atom from the best-fit plane being 0.0045 (13) Å for the C1–C6 ring and 0.0065 (12) Å for the C12–C17 ring, while the average deviations are 0.0029 (12) and 0.003 (2) Å, respectively. The dihedral angle between the best-fit planes of these rings, the biphenyl twist angle, is 79.95 (6)°. This value may be compared with that observed for the dimethyl ester of a similar 6,6′-substituted biphenyl-2,2′-dicarboxylic acid, dimethyl 6,6′-dimethoxy-3,3′,5,5′-tetramethylbiphenyl-2,2′-dicarboxylate [hereafter, (II)] (Dobson & Gerkin, 1999), 71.3 (1)°; the mean deviation of the ring-C atoms in (II) from these planes is 0.008 (4) Å. In (I), the torsion angles C2—C1—C12—C13 and C2—C1—C12—C17 measure −81.6 (2) and 98.0 (2)°, respectively. The dihedral angle between the C7/O1/O2 plane and that of the phenyl ring to which it is attached is 23.0 (2)°; the corresponding dihedral angle involving the C18/O3/O4 plane is 28.8 (2)°. These values contrast strongly with the corresponding value observed for (II), 62.3 (2)°, but this is not inconsistent with differences in the ester groups and adjacent substituents on the rings in the two molecules.

Selected bond distances and angles for (I) are given in Table 1. All distances and angles fall within normal limits. In (I), the several closest intermolecular approaches, excluding pairs of atoms involved in the tabulated C—H···O interactions, exceed (but by statistically insignificant amounts) the corresponding Bondi (1964) van der Waals radius sums.

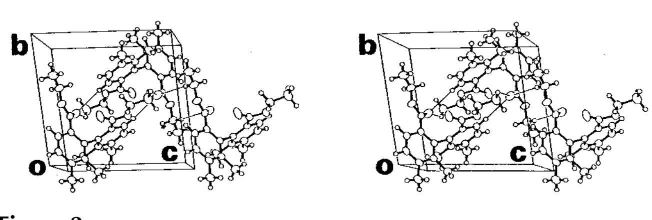


Figure 2
Stereopacking diagram of (I) viewed almost along the *a* axis. The finer interatomic lines depict the tabulated interactions.

Experimental

Compound (I) was obtained as a large, colorless slab from a sample in the chemical collection of Dr M. S. Newman. This was cut to provide the experimental sample. A synthesis is described by Newman & Lilje (1979).

Crystal data

$C_{22}H_{26}O_4$
$M_r = 354.45$
Triclinic, $P\overline{1}$
$a = 8.9719$ (2) Å
$b = 10.7632$ (2) Å
$c = 10.8399$ (2) Å
$\alpha = 92.9965$ (10)°
$\beta = 90.1788$ (10)°
$\gamma = 113.3672$ (9)°
$V = 959.28$ (3) Å^3

$Z = 2$
$D_x = 1.227$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 22068 reflections
$\theta = 2.06$–27.52°
$\mu = 0.083$ mm^{-1}
$T = 193$ K
Cut slab, colorless
0.42 × 0.35 × 0.27 mm

Data collection

Nonius KappaCCD diffractometer
ω scans with κ offsets
22068 measured reflections
4374 independent reflections
3340 reflections with $I > 2\sigma_I$

$R_{\rm int} = 0.024$
$\theta_{\rm max} = 27.52°$
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R(F) = 0.050$
$wR(F^2) = 0.125$
$S = 1.94$
4374 reflections
323 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2_{\rm cs} + (0.035I)^2]$
$(\Delta/\sigma)_{\rm max} = 0.0003$
$\Delta\rho_{\rm max} = 0.33$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C7	1.3357 (14)	O3—C18	1.3422 (15)
O1—C10	1.4534 (15)	O3—C21	1.4487 (17)
O2—C7	1.2025 (15)	O4—C18	1.2024 (15)
C7—O1—C10	116.83 (10)	O1—C10—C11	107.50 (12)
C18—O3—C21	115.79 (10)	O3—C18—O4	122.86 (12)
O1—C7—O2	122.64 (11)	O3—C18—C13	111.66 (10)
O1—C7—C2	111.33 (10)	O4—C18—C13	125.47 (12)
O2—C7—C2	126.00 (11)	O3—C21—C22	107.50 (14)

Table 2
Leading C—H···O interactions (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···O4$^{\rm i}$	0.98	2.71	3.671 (2)	167
C11—H11B···O4$^{\rm i}$	0.98 (2)	2.73 (2)	3.511 (2)	137.0 (15)
C21—H21B···O4$^{\rm ii}$	0.94 (2)	2.71 (2)	3.625 (2)	163.1 (12)

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

Table 3
Basic first- and second-level graph-set descriptors involving interactions designated *a*–*c* in the order as given in Table 2.

	a	*b*	*c*
a	$R_2^2(16)$	$R_2^1(9)$	$C_2^1(11)$
b		$R_2^2(22)$	$C_2^1(14)$
c			$R_2^2(10)$

Fourier difference methods were used to locate initial H-atom positions and all H atoms were refined. The four ring H atoms were then made canonical, with C—H = 0.98 Å and $U_{\rm iso} = 1.2 \times U_{\rm eq}$ of the attached C atom. The range of the 22 refined C—H distances is 0.92 (2)–1.05 (2) Å, and the mean value is 0.98 (4) Å.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1995); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

I acknowledge with pleasure my use of the departmental X-ray crystallographic facility, which is supervised by staff crystallographer Dr J. C. Gallucci.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1277). Services for accessing these data are described at the back of the journal.

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