Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

1-Ethyl 2,2-dimethyl 3-(1,3-benzodioxol-5-yl)propane-1,2,2-tricarboxylate

Bruce A. Hathaway,* Uriah J. Kilgore and Marcus R. Bond

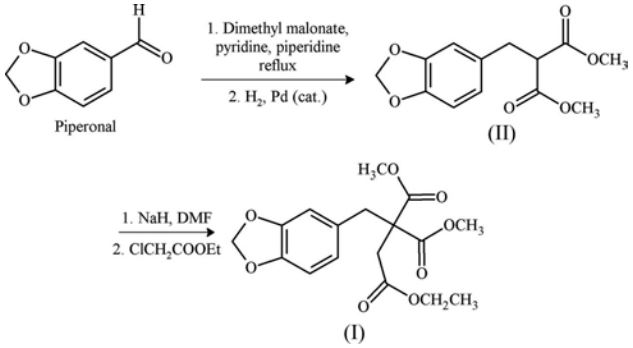
Department of Chemistry, Southeast Missouri State University, Cape Girardeau, MO 63701, USA
Correspondence e-mail: bahathaway@semo.edu

Received 29 March 2008
Accepted 9 July 2008
Online 19 July 2008

The molecular structure of the title triester compound, $C_{17}H_{20}O_8$, consists of a benzodioxole fused-ring system, an ethoxycarbonylmethyl group and two methoxycarbonyl groups arranged around a tetrahedral carbon center. Unlike similar triesters, which are oils, the title compound crystallizes at room temperature as interdigitated bilayers of triester molecules, with short O···H contacts from the methylene H atoms of benzodioxole to the carbonyl O atom of the ethoxycarbonylmethyl group and to a ring O atom of the benzodioxole group of a neighboring molecule within the bilayer. The persistence of these short C—H···O interactions from the activated H atoms of the benzodioxole ring at both 100 and 300 K indicate that they help provide the stabilization necessary for crystallization from the oil.

Comment

The title compound, (I), was prepared in the course of preparation of analogs of 1,2-dihydronaphthalen-2-amine (Hathaway *et al.*, 1982). Unlike similar triesters, which are oils, the title compound crystallized at room temperature. It was prepared from dimethyl (1,3-benzodioxol-5-ylmethyl)malonate, (II), by alkylation with ethyl chloroacetate. The starting compound, (II), was prepared from piperonal (see scheme).



While the following details, as well as the figures and bond-length table, are derived from the structure at 100 K, similar geometry is found for the room-temperature structure, except where otherwise noted.

The benzodioxole fused-ring system, two methoxycarbonyl groups, and an ethoxycarbonylmethyl group are arranged around the tetrahedral C2 atom. Bond lengths and angles within the six-membered ring are consistent with its aromatic character, although significant bond-length alternation is found. The C33—C34 bond length of 1.3848 (17) Å for the two ring C atoms that are also part of the five-membered ring is close in value to the average C—C bond length in the six-

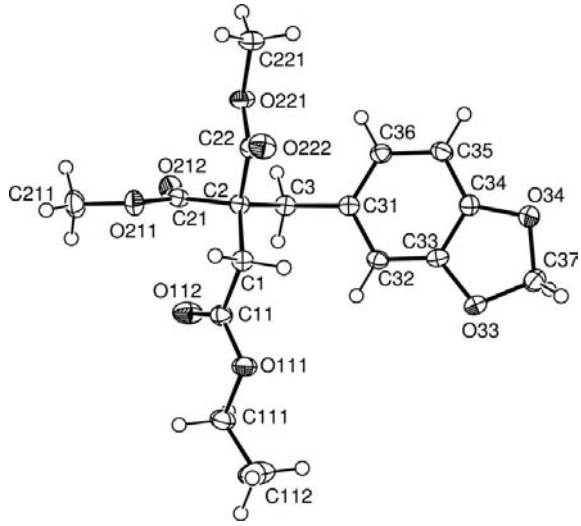


Figure 1
The title compound (T = 100 K), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

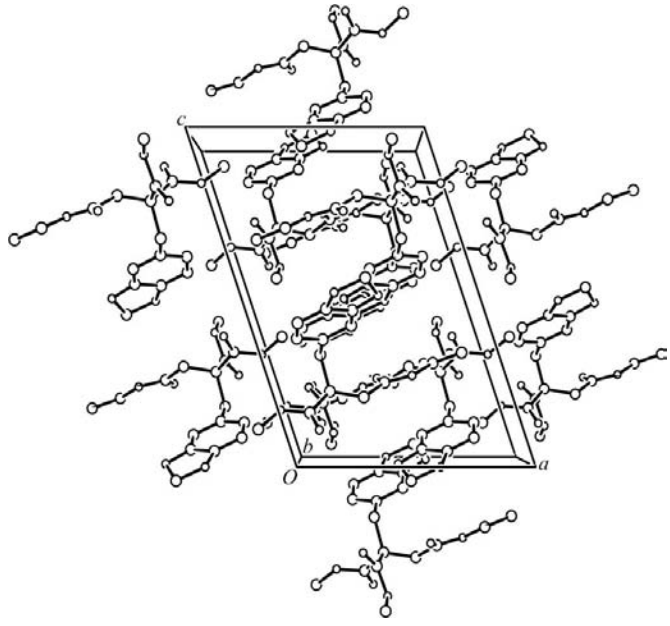


Figure 2
The packing of the title compound at 100 K. The bilayer structure is shown within the unit cell boundaries, with molecules from neighboring layers shown to the left and right.

  doi:10.1107/S0108270108021392

membered ring (1.390 Å). The two neighboring bonds (C32—C33 and C34—C35) have the shortest lengths in the ring (Table 1), while the next two neighboring bonds (C31—C32 and C35—C36) are the longest; the opposite bond in the ring (C31—C36) is again close to the average.

The gross shape of the molecule is flattened with respect to the tetrahedron about C2 and, in the projection of Fig. 1, can be viewed as being formed by intersecting diester and monoester chains, both with an *anti* conformation, which cross at approximately a right angle [87.84 (4)° between their mean planes] and share C2. The diester chain, which extends from the ethoxy group (C112) to the C221 methoxy group, exhibits a significant twist, with the ethoxy-group plane forming an angle of 28.40 (6)° relative to the plane of the remaining atoms in this chain. The monoester chain runs from the fused-ring system to the C211 methoxy group. The fused-ring system is almost coplanar with the mean plane of the molecule [dihedral angle = 13.34 (3)°] and forms an angle of 76.72 (3)° with the plane of the monoester chain.

The extended structure consists of interdigitated bilayers of the title molecule parallel to the crystallographic *bc* plane (Fig. 2). The ethoxy chain and benzodioxole ring of each molecule are directed into the bilayer such that the ethoxy chain of one molecule lies between benzodioxole rings of two neighbors and *vice versa*. Shortest O···H contact distances between neighboring molecules are 2.48 Å [O112···H37A^{i}; symmetry code: (i) $1-x, 1-y, 1-z$], linking the carbonyl O atom of the ethoxy group to a methylene H atom of the benzodioxole group, and 2.52 Å [O34···H37B^{ii}; symmetry code: (ii) $1-x, -y, 1-z$] linking an O atom of the benzodioxole group to the other methylene H atom within the bilayer in the 300 K structure. These contacts decrease in length to 2.355 (15) and 2.406 (15) Å, respectively, at 100 K. Since atom C37 is bound to two O atoms, it is not surprising that the H atoms attached to it would be activated.

One methoxy group (C211) is approximately parallel with, and on the outer edges of, the bilayer. The other methoxy group (C221) is approximately perpendicular to the bilayer and partially extends into the neighboring bilayer. The short C—H···O hydrogen bonds that link neighboring molecules within the layer and the enhanced dispersion forces arising from partial extension of ethoxy groups into neighboring layers likely provide the stabilization needed for the compound to crystallize from the oil.

Experimental

To a solution of (II) (10.6 g, 0.040 mol) in *N*,*N*-dimethylformamide (DMF, 30 ml) under nitrogen was added sodium hydride (50% in mineral oil; 1.92 g, 0.040 mol). The resulting red solution was stirred for 45 min, after which a solution of ethyl chloroacetate (4.9 g, 0.040 mol) in DMF (10 ml) was added dropwise over a period of 10 min. The resulting solution was heated at 333 K overnight. The reaction mixture was poured into water (100 ml), and extracted three times with ether. The combined ether layers were dried with magnesium sulfate, and the solvent removed under reduced pressure. The residual yellow oil was dissolved in acetonitrile, and the acetonitrile was washed twice with hexane. The acetonitrile was removed under reduced pressure to produce the title compound as a yellow oil, which crystallized upon standing (yield 9.11 g, 65%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.27 (*t*, 3H, *J* = 7.1 Hz, H112), 2.86 (*s*, 2H, H1), 3.30 (*s*, 2H, H3), 3.76 (*s*, 6H, OCH_3), 4.16 (*q*, 2H, *J* = 7.1 Hz, H111), 5.93 (*s*, 2H, H37), 6.52 (*dd*, 1H, *J* = 7.9 and 2.7 Hz, H36), 6.56 (*d*, 1H, *J* = 2.7 Hz, H32) and 6.71 (*d*, 1H, *J* = 7.9 Hz, H35). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 14.1 (C112), 36.8 (C3), 38.5 (C1), 52.8 (OCH_3), 56.8 (C2), 60.8 (C111), 101.0 (C37), 108.2 (C32 or C35), 110.2 (C32 or C35), 123.2 (C36), 129.0 (C31), 146.8 (C33 or C34), 147.6 (C33 or C34), 170.4 (C21 and C22) and 170.6 (C11).

Compound (I) at 100 K

Crystal data

$C_{17}H_{20}O_8$
M_r = 352.33
Monoclinic, $P2_1/c$
a = 10.3799 (2) Å
b = 11.7642 (2) Å
c = 14.5275 (3) Å
β = 109.4783 (8)°
V = 1672.49 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 100 (2) K
0.30 × 0.30 × 0.25 mm

Data collection

Nonius KappaCCD diffractometer
4861 measured reflections
4861 independent reflections
3573 reflections with $I > 2\sigma(I)$
R_{int} = 0.051

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.108
S = 1.05
4861 reflections
306 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Compound (I) at 300 K

Crystal data

$C_{17}H_{20}O_8$
M_r = 352.34
Monoclinic, $P2_1/c$
a = 10.4985 (2) Å
b = 11.8828 (2) Å
c = 14.7540 (3) Å
β = 109.5329 (9)°
V = 1734.66 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 300 (2) K
0.30 × 0.30 × 0.25 mm

Data collection

Nonius KappaCCD diffractometer
6310 measured reflections
3157 independent reflections
1879 reflections with $I > 2\sigma(I)$
R_{int} = 0.047

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.144
S = 1.05
3157 reflections
228 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

For *T* = 100 K, all H atoms were found in difference maps and freely refined. Refined C—H bond lengths range from 0.953 (14) to 1.07 (3) Å. All of the H atoms in the 300 K structure were visible in difference maps, except for those of two of the methyl groups (C112 and C211), for which only some of the H atoms were visible. All H-atom positions were calculated to give an idealized geometry about

Table 1
Selected bond lengths (Å) for (I) at 100 K.

C1—C2	1.5361 (16)	C33—C34	1.3848 (17)
C2—C3	1.5531 (16)	C34—C35	1.3739 (17)
C31—C36	1.3940 (17)	C34—O34	1.3792 (15)
C31—C32	1.4101 (17)	C35—C36	1.4050 (18)
C32—C33	1.3737 (18)	O33—C37	1.4339 (16)
C33—O33	1.3752 (14)	O34—C37	1.4407 (16)

their parent atoms in the 300 K structure. Multiple difference-map peaks around the C112 and C211 methyl groups implied disorder and H-atom positions were calculated to give twofold disorder. The torsion angle of the methyl group at C221 was refined to match the electron density. Calculated C—H bond lengths in the 300 K structure are assigned in the range 0.96–0.97 Å for methyl and methylene H atoms and 0.93 Å for aromatic H atoms.

For both determinations, data collection: *COLLECT* (Hooft, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *maXus* (Mackay *et al.*, 1999) and *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP* (Johnson, 1976); software used to prepare material for publication: *PARST* (Nardelli, 1995).

The authors thank the National Science Foundation DUE CCLI–A&I program (grant No. 9951348) and Southeast Missouri State University for funding the X-ray diffraction facility.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3145). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Hathaway, B. A., Nichols, D. E., Nichols, M. B. & Yim, G. K. W. (1982). *J. Med. Chem.* **25**, 535–538.
Hooft, R. W. W. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Mackay, S., Gilmore, C. J., Edwards, C., Stewart, N. & Shankland, K. (1999). *maXus*. Nonius BV, Delft, The Netherlands, MacScience Co. Ltd, Japan, and The University of Glasgow, Scotland.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.