organic compounds

Diethyl 2,2′-(ethane-1,2-diyldioxy)di-benzoate

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The molecular title compound, $C_{20}H_{22}O_6$, was obtained by the reaction of ethyl 2-hydroxybenzoate with 1,2-dichloroethane. The molecule lies on a twofold rotation axis which passes through the middle of the central ethylene bridge. This group exhibits a *gauche* conformation with the corresponding O—C—C—O torsion angle being 73.2 (2)°. The C atoms of the carboxyl group, the aryl and the O—CH_2 group are coplanar, with an r.m.s. deviation of 0.01 Å. The two aryl rings form a dihedral angle of 67.94 (4)°. The ester ethyl group is disordered over two sets of sites with an occupancy ratio of 0.59 (2):0.41 (2). The crystal packing is dominated by van der Waals forces.

Related literature

For synthesis and structures of diesters, see: Ma *et al.* (2012); Hou & Kan (2007). For properties and applications of diesters, see: Chen & Liu (2002). For the synthesis of the title compound, see: Ma & Liu (2002). For standard bond lengths, see: Allen *et al.* (1987). For background to the applications of organic acids and esters, see: Chanthapally *et al.* (2012); Yan *et al.* (2012).
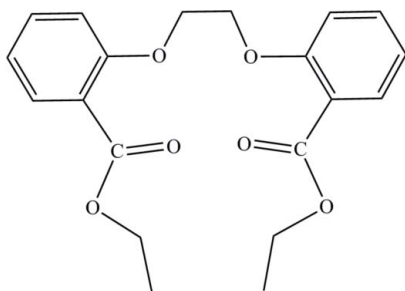
Experimental

Crystal data

$C_{20}H_{22}O_6$	V = 1908.0 (6) Å^3
M_r = 358.38	Z = 4
Orthorhombic, $Pbcn$	Mo $K\alpha$ radiation
a = 21.805 (4) Å	μ = 0.09 mm^{-1}
b = 9.871 (2) Å	T = 298 K
c = 8.8646 (18) Å	0.35 × 0.31 × 0.28 mm

Data collection

Bruker SMART CCD diffractometer	11280 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)	2192 independent reflections
T_{min} = 0.858, T_{max} = 1.000	1543 reflections with $I > 2\sigma(I)$
	R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041	24 restraints
$wR(F^2)$ = 0.132	H-atom parameters constrained
S = 1.04	$\Delta\rho_{max}$ = 0.17 e Å^{-3}
2192 reflections	$\Delta\rho_{min}$ = −0.14 e Å^{-3}
140 parameters	

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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supporting information

Diethyl 2,2′-(ethane-1,2-diyldioxy)dibenzoate

Huaduan Shi, Haisha Qin and Zhen Ma

S1. Comment

In recent years the chemistry of carboxylic compounds has been the subject of intense studies because of the potential applications of these compounds as ligands for metal complexes or of potential applications as luminescent, non-linear optical, electrical conductive and liquid-crystalline materials (Yan *et al.*, 2012. Chanthapally *et al.*, 2012). Esters are also very important since these compounds are commodity chemicals used as intermediates in the manufacture of acids and in the production of numerous important industrial products. Hence, the current work aims to synthesize new esters for acid production and for investigation of their coordination behaviors with metal ions (Ma *et al.*, 2012; Chen & Liu, 2002). Here, we report the crystal structure of a new diester, $C_{20}H_{22}O_6$, which was obtained by reaction of ethyl 2-hydroxy-benzoate with 1,2-dichloroethane.

The structure of $C_{20}H_{22}O_6$ consists of a neutral molecular unit (Fig. 1). The molecule lies on a twofold rotation axis which passes through the middle of the central ethylene bridge that has a *gauche* conformation with the corresponding O—C—C—O torsion angle being 73.2 (2) °. All bond lengths and angles are within normal ranges (Allen *et al.*, 1987). The carbon atom of the carboxyl group, and the aryl and O—CH_2 moeities of one half molecule are coplanar with an r.m.s. deviation of 0.01 Å. The two aryl rings form a dihedral angle of 67.94 (4) °. The ester ethyl group is disordered over two sets of sites in a 0.59 (2):0.41 (2) occupancy ratio. The packing of the molecules in the crystal structure is shown in Fig. 2.

S2. Experimental

The title compound was obtained by the reaction of ethyl 2- hydroxybenzoate with 1,2-dichloroethane in *N,N′*- dimethyl-formamide (DMF) according to a reported procedure (Ma & Liu, 2002). In a 100 cm^3 flask fitted with a funnel, ethyl 2-hydroxybenzoate (8.3 g, 50 m*M*) and potassium carbonate were mixed in 50 cm^3 of DMF. To this solution was added dropwise a stoichiometric quantity of 1,2-dichloroethane (2.5 g, 25 m*M*) dissolved in 20 cm^3 of DMF for a period of an hour under stirring. The mixture was further stirred for 24 h at 353 K. The solution was concentrated under reduced pressure and the white solid precipitated by adding a large quantity of water (200 cm^3) was filtered off and recrystallized from ethanol and decolored with activated carbon. A colorless solid was finally obtained (yield 81 %, m.p: 417–419 K). Slow evaporation of a solution of the title compound in ethanol and dichloromethane (1:1) led to the formation of colorless crystals, which were suitable for X-ray characterization.

S3. Refinement

All H atoms were positioned geometrically and refined using a riding model with C—H = 0.93 - 0.97 Å and with $U_{iso}(H)$ = 1.2 times $U_{eq}(C)$ or 1.5 times U_{eq} (methyl C). The two carbon atoms of the ethyl group are disordered over two sets of sites with an occupancy ratio of 0.59 (2):0.41 (2). The C atoms of this group were additionally refined with the ISOR command in SHELXL.
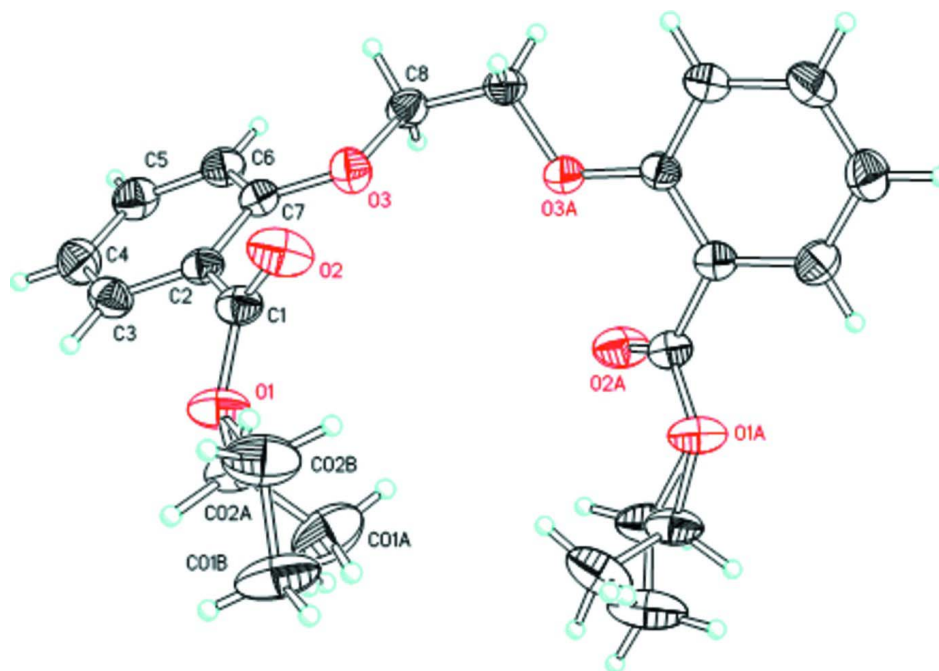
Figure 1

The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are presented as small spheres of arbitrary radius. [symmetry code: (A) 1-*x*, *y*, 1/2-*z*]
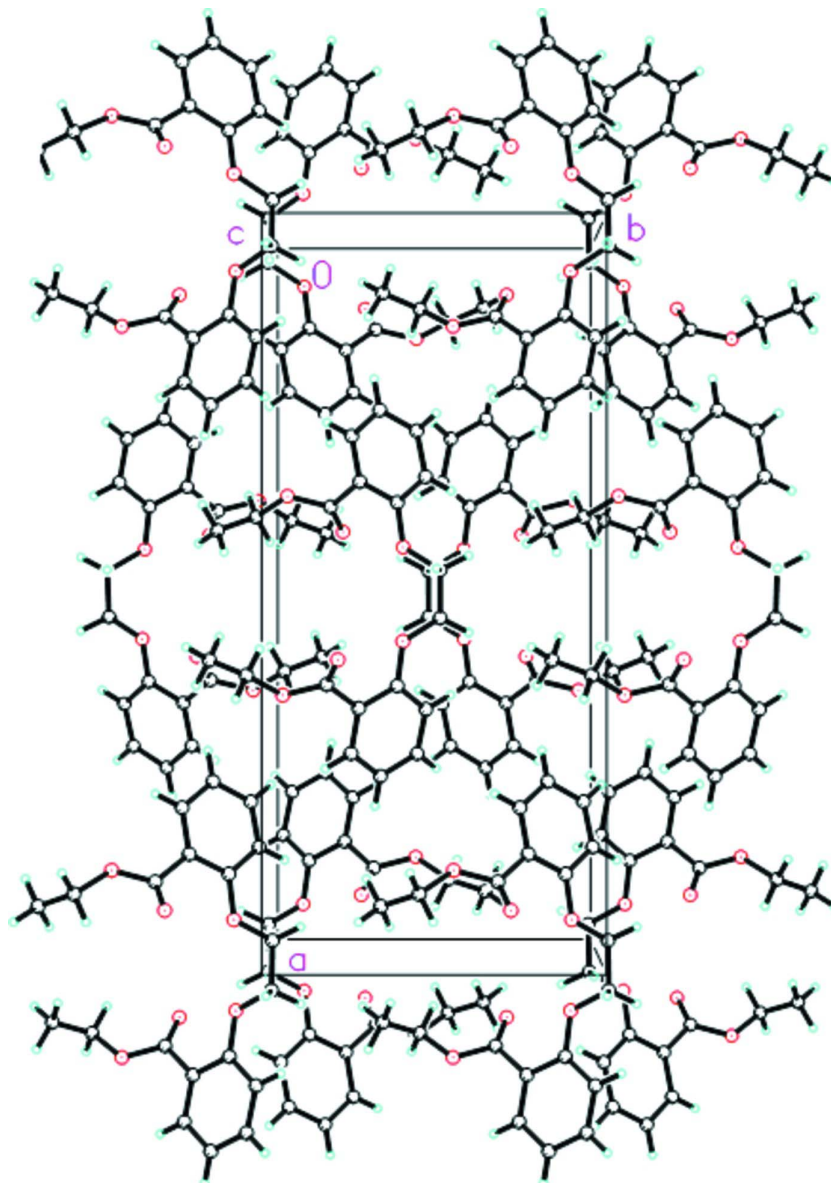
Figure 2

A view of the crystal packing along the *c* axis.

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Crystal data

$C_{20}H_{22}O_6$	$F(000) = 760$
$M_r = 358.38$	$D_x = 1.248$ Mg m^{-3}
Orthorhombic, *Pbcn*	Mo *Kα* radiation, $λ = 0.71073$ Å
Hall symbol: -P 2n 2ab	Cell parameters from 11280 reflections
$a = 21.805$ (4) Å	$θ = 1.9–27.6°$
$b = 9.871$ (2) Å	$μ = 0.09$ mm^{-1}
$c = 8.8646$ (18) Å	$T = 298$ K
$V = 1908.0$ (6) Å^3	Prism, colourless
$Z = 4$	$0.35 × 0.31 × 0.28$ mm

Data collection

Bruker SMART CCD diffractometer	11280 measured reflections
Radiation source: fine-focus sealed tube	2192 independent reflections
Graphite monochromator	1543 reflections with $I > 2\sigma(I)$
Detector resolution: 0 pixels mm^{-1}	$R_{int} = 0.023$
phi and ω scans	$\theta_{max} = 27.6°$, $\theta_{min} = 1.9°$
Absorption correction: multi-scan	$h = -28\rightarrow27$
(*SADABS*; Bruker, 2002)	$k = -10\rightarrow12$
$T_{min} = 0.858$, $T_{max} = 1.000$	$l = -10\rightarrow11$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.041$	$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 0.335P]$
$wR(F^2) = 0.132$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
2192 reflections	$\Delta\rho_{max} = 0.17$ e Å^{-3}
140 parameters	$\Delta\rho_{min} = -0.14$ e Å^{-3}
24 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0102 (19)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.36609 (7)	0.94335 (11)	0.09160 (14)	0.0784 (4)	
O2	0.41410 (7)	0.77861 (13)	−0.03024 (15)	0.0880 (5)	
O3	0.43658 (5)	0.59258 (11)	0.20505 (13)	0.0632 (3)	
C1	0.38057 (7)	0.81417 (15)	0.06775 (17)	0.0570 (4)	
C02A	0.3859 (9)	1.0477 (15)	−0.0051 (11)	0.075 (3)	0.41 (2)
H02A	0.4024	1.0099	−0.0976	0.090*	0.41 (2)
H02B	0.3518	1.1066	−0.0307	0.090*	0.41 (2)
C02B	0.4008 (7)	1.0397 (13)	−0.0105 (13)	0.114 (4)	0.59 (2)
H02C	0.4421	1.0064	−0.0273	0.137*	0.59 (2)
H02D	0.3804	1.0466	−0.1074	0.137*	0.59 (2)
C2	0.34747 (7)	0.72278 (14)	0.17329 (15)	0.0522 (4)	
C01A	0.4309 (8)	1.120 (2)	0.0708 (15)	0.127 (4)	0.41 (2)
H01A	0.4127	1.1683	0.1536	0.191*	0.41 (2)
H01B	0.4497	1.1835	0.0029	0.191*	0.41 (2)

H01C	0.4614	1.0587	0.1084	0.191*	0.41 (2)
C01B	0.4030 (7)	1.1719 (7)	0.0618 (8)	0.119 (3)	0.59 (2)
H01D	0.3620	1.2059	0.0738	0.179*	0.59 (2)
H01E	0.4262	1.2333	0.0004	0.179*	0.59 (2)
H01F	0.4220	1.1637	0.1590	0.179*	0.59 (2)
C3	0.28631 (8)	0.74645 (17)	0.20651 (18)	0.0654 (4)	
H3A	0.2668	0.8215	0.1650	0.078*	
C4	0.25382 (8)	0.6610 (2)	0.3000 (2)	0.0766 (5)	
H4A	0.2126	0.6773	0.3198	0.092*	
C5	0.28283 (8)	0.55161 (18)	0.3634 (2)	0.0730 (5)	
H5A	0.2611	0.4946	0.4275	0.088*	
C6	0.34359 (7)	0.52495 (15)	0.33381 (19)	0.0634 (4)	
H6A	0.3627	0.4505	0.3778	0.076*	
C7	0.37642 (7)	0.60994 (14)	0.23769 (16)	0.0518 (4)	
C8	0.46777 (7)	0.48215 (15)	0.27597 (19)	0.0609 (4)	
H8A	0.4482	0.3972	0.2493	0.073*	
H8B	0.4662	0.4922	0.3848	0.073*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.1251 (11)	0.0471 (6)	0.0631 (7)	0.0001 (6)	0.0089 (7)	0.0031 (5)
O2	0.1222 (11)	0.0685 (8)	0.0732 (8)	0.0098 (7)	0.0363 (8)	0.0084 (6)
O3	0.0597 (6)	0.0607 (6)	0.0692 (7)	0.0009 (5)	0.0008 (5)	0.0183 (5)
C1	0.0753 (9)	0.0505 (8)	0.0451 (7)	0.0019 (7)	−0.0047 (7)	−0.0018 (6)
C02A	0.128 (7)	0.054 (4)	0.043 (3)	−0.014 (4)	−0.014 (4)	0.008 (3)
C02B	0.174 (9)	0.065 (4)	0.104 (6)	−0.006 (4)	0.034 (5)	0.020 (4)
C2	0.0654 (9)	0.0485 (7)	0.0425 (7)	−0.0015 (6)	−0.0024 (6)	−0.0060 (6)
C01A	0.146 (10)	0.103 (9)	0.133 (7)	−0.059 (7)	0.022 (6)	0.010 (7)
C01B	0.228 (10)	0.057 (3)	0.073 (3)	−0.031 (4)	−0.001 (4)	0.003 (2)
C3	0.0717 (10)	0.0647 (9)	0.0597 (9)	0.0118 (8)	0.0008 (8)	−0.0057 (8)
C4	0.0655 (10)	0.0869 (12)	0.0774 (12)	−0.0004 (9)	0.0129 (9)	−0.0070 (10)
C5	0.0767 (11)	0.0687 (10)	0.0735 (11)	−0.0147 (9)	0.0173 (9)	0.0001 (9)
C6	0.0733 (10)	0.0530 (8)	0.0640 (9)	−0.0065 (7)	0.0039 (8)	0.0054 (7)
C7	0.0580 (8)	0.0487 (7)	0.0488 (8)	−0.0043 (6)	−0.0011 (6)	−0.0018 (6)
C8	0.0677 (8)	0.0487 (8)	0.0662 (9)	−0.0034 (7)	−0.0087 (7)	0.0060 (7)

Geometric parameters (Å, º)

O1—C1	1.3306 (18)	C01A—H01B	0.9600
O1—C02A	1.408 (14)	C01A—H01C	0.9600
O1—C02B	1.516 (14)	C01B—H01D	0.9600
O2—C1	1.1884 (19)	C01B—H01E	0.9600
O3—C7	1.3541 (18)	C01B—H01F	0.9600
O3—C8	1.4304 (17)	C3—C4	1.379 (2)
C1—C2	1.487 (2)	C3—H3A	0.9300
C02A—C01A	1.39 (2)	C4—C5	1.372 (3)
C02A—H02A	0.9700	C4—H4A	0.9300

C02A—H02B	0.9700	C5—C6	1.376 (2)
C02B—C01B	1.455 (15)	C5—H5A	0.9300
C02B—H02C	0.9700	C6—C7	1.394 (2)
C02B—H02D	0.9700	C6—H6A	0.9300
C2—C3	1.386 (2)	C8—C8i	1.479 (3)
C2—C7	1.402 (2)	C8—H8A	0.9700
C01A—H01A	0.9600	C8—H8B	0.9700
C1—O1—C02A	122.1 (7)	C02B—C01B—H01F	109.5
C1—O1—C02B	112.8 (5)	H01D—C01B—H01F	109.5
C02A—O1—C02B	12.6 (12)	H01E—C01B—H01F	109.5
C7—O3—C8	117.59 (11)	C4—C3—C2	121.27 (16)
O2—C1—O1	123.04 (15)	C4—C3—H3A	119.4
O2—C1—C2	125.41 (14)	C2—C3—H3A	119.4
O1—C1—C2	111.49 (13)	C5—C4—C3	119.41 (16)
C01A—C02A—O1	107.4 (10)	C5—C4—H4A	120.3
C01A—C02A—H02A	110.2	C3—C4—H4A	120.3
O1—C02A—H02A	110.2	C4—C5—C6	121.09 (16)
C01A—C02A—H02B	110.2	C4—C5—H5A	119.5
O1—C02A—H02B	110.2	C6—C5—H5A	119.5
H02A—C02A—H02B	108.5	C5—C6—C7	119.74 (15)
C01B—C02B—O1	108.4 (10)	C5—C6—H6A	120.1
C01B—C02B—H02C	110.0	C7—C6—H6A	120.1
O1—C02B—H02C	110.0	O3—C7—C6	123.51 (13)
C01B—C02B—H02D	110.0	O3—C7—C2	116.73 (12)
O1—C02B—H02D	110.0	C6—C7—C2	119.73 (14)
H02C—C02B—H02D	108.4	O3—C8—C8i	108.37 (12)
C3—C2—C7	118.74 (14)	O3—C8—H8A	110.0
C3—C2—C1	119.91 (13)	C8i—C8—H8A	110.0
C7—C2—C1	121.32 (13)	O3—C8—H8B	110.0
C02B—C01B—H01D	109.5	C8i—C8—H8B	110.0
C02B—C01B—H01E	109.5	H8A—C8—H8B	108.4
H01D—C01B—H01E	109.5		
C02A—O1—C1—O2	4.9 (7)	C1—C2—C3—C4	177.81 (15)
C02B—O1—C1—O2	−4.7 (6)	C2—C3—C4—C5	1.1 (3)
C02A—O1—C1—C2	−172.4 (7)	C3—C4—C5—C6	−0.8 (3)
C02B—O1—C1—C2	177.9 (6)	C4—C5—C6—C7	−0.1 (3)
C1—O1—C02A—C01A	−107.6 (14)	C8—O3—C7—C6	−1.2 (2)
C02B—O1—C02A—C01A	−63 (4)	C8—O3—C7—C2	176.78 (13)
C1—O1—C02B—C01B	−156.1 (10)	C5—C6—C7—O3	178.61 (15)
C02A—O1—C02B—C01B	64 (4)	C5—C6—C7—C2	0.7 (2)
O2—C1—C2—C3	−136.02 (18)	C3—C2—C7—O3	−178.45 (13)
O1—C1—C2—C3	41.24 (19)	C1—C2—C7—O3	3.3 (2)
O2—C1—C2—C7	42.3 (2)	C3—C2—C7—C6	−0.4 (2)

| O1—C1—C2—C7 | −140.48 (14) | C1—C2—C7—C6 | −178.72 (13) |
| C7—C2—C3—C4 | −0.5 (2) | C7—O3—C8—C8ⁱ | 179.76 (14) |

Symmetry code: (i) −*x*+1, *y*, −*z*+1/2.