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Diethyl 4,4′-[octane-1,8-diylbis(oxy)]dibenzoate

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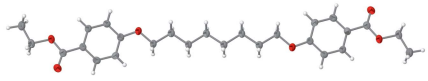
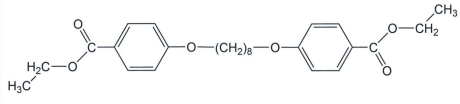
The complete molecule of the title compound, $C_{26}H_{34}O_6$, is generated by a crystallographic centre of symmetry and the central octyl chain adopts an extended conformation. In the extended structure, weak C—H$\cdots\pi$ interactions link the molecules.

3D view



Chemical scheme



Structure description

Alkylbenzoates possess interesting physical properties and applications in industry. For example, 4-hydroxybenzoic acid and its esters are known as parabens (Giordano *et al.*, 1999; Yang *et al.*, 2014), and alkylbenzoates are used for preparing liquid crystalline compounds (Abser *et al.*, 1993), and non-linear optical materials (Perumal *et al.*, 2002). As part of our studies in this area, we now describe the synthesis and structure of the title compound, $C_{26}H_{34}O_6$ (Fig. 1).

The X-ray diffraction analysis revealed that the title molecule is centrosymmmetric with the inversion center located in the middle of the alkyl chain. The mean plane through the non-hydrogen atoms indicates that they are almost coplanar with r.m.s. and maximum deviations of 0.101 and ±0.151 (2) Å (exhibited by atom C6), respectively. The *n*-octyl alkyl chain exhibits an extended (all *anti*) conformation. The bond distances agree with those reported in similar compounds (Ma *et al.*, 2011, 2012; Shi *et al.*, 2014). The crystal packing shows the molecules connected by C3—H3*A*$\cdots\pi$ and C12—H12*B*$\cdots\pi$ interactions with H–ring centroid separations of 2.89 and 2.82 Å, respectively (Table 1, Fig. 2).

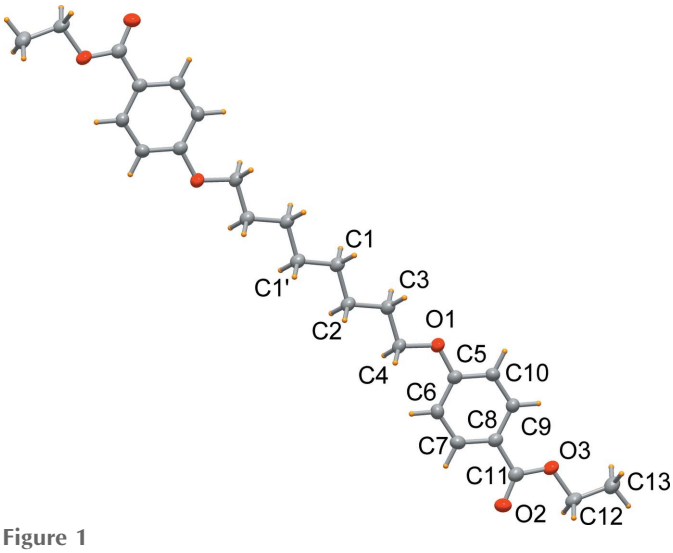


Figure 1
ORTEP view (ellipsoids drawn at the 50% probability level) of the title molecule. C1′ and unlabelled atoms are generated by the symmetry operation $-x + 2, -y + 2, -z$.

Synthesis and crystallization

A mixture of ethyl-4-hydroxybenzoate (8.3 g, 50 mmol) and 1,8-dibromo-octane (6.8 g, 25 mmol) in acetone (100 ml) was refluxed for 24 h over anhydrous potassium carbonate (13.8 g, 100 mmol). The solvent was removed under vacuum and the solid mass was dissolved in water and extracted with dichloromethane. Left overnight, a white precipitate formed, which was filtered off and washed with ethanol. The product was recrystallized from hot ethanol solution, resulting in colorless needle-shaped crystals suitable for X-ray diffraction. Yield: 9.6 g (86%), melting point: 372–373 K.

FT–IR (KBr), (cm^{-1}): 1707 ν (C═O_{ester}), 1606, 1580 ν (C═$C_{aromatic}$), 3072, 3052 ν (C—$H_{aromatic}$), 2914, 2942, 2874, 2858 ν (C—$H_{aliphatic}$).

^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.99 (d, 2 × 2H, J = 8.8 Hz, C-2,6,2′,6′), 6.90 (d, 2 × 2H, J = 8.8 Hz, C-3,5,3′,5′), 4.35 (q, 2 × 2H, OCH_2CH_3), 4.0 (t, 2 × 2H, J = 7.6 Hz, OCH_2CH_2), 1.81 (p, 2 × 2H, OCH_2CH_2), 1.5 (p, 2 × 2H, $OCH_2CH_2CH_2$), 1.41 (p, 2 × 2H, $OCH_2CH_2CH_2CH_2$), 1.40 (t, 2 × 3H, CH_3).

^{13}C NMR ($CDCl_3$, 400 MHz), δ: 14.47 (2 C, CH_3), 26.00 (2 C, $OCH_2CH_2CH_2CH_2$), 29.17 (2 C, $OCH_2CH_2CH_2$), 29.33 (2 C, OCH_2CH_2), 60.67 (2 C, OCH_2CH_2), 68.13 (2 C, OCH_2CH_3), 122.78 (2 C, C-4,4′), 163 (2 C, C-1,1′), 114 (2 × 2 C, C-3,5,3′,5′), 131.59 (2 × 2 C, C-2,6,2′,6′), 166.51 (2 C, OCO)

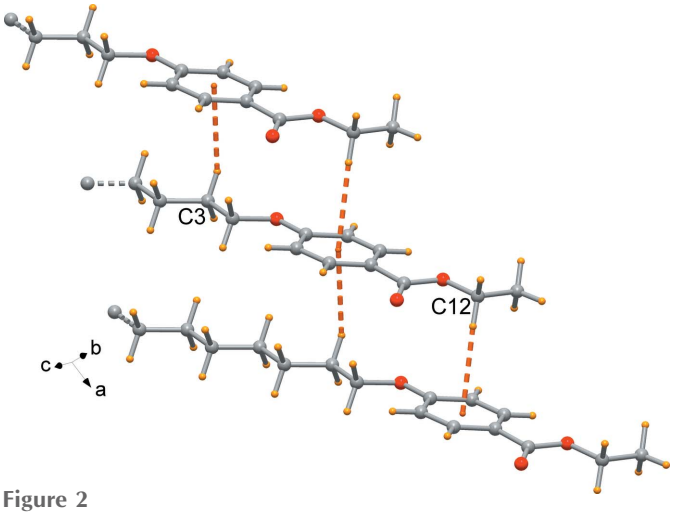


Figure 2
Detail of the crystal packing showing the C—H···π interactions.

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

*Cg*1 is the centroid of the C5–C10 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3A···$Cg1^{i}$	0.99	2.89	3.728 (2)	143
C12—H12B···$Cg1^{ii}$	0.99	2.82	3.744 (2)	155

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{26}H_{34}O_6$
M_r	442.53
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	173
a, b, c (Å)	6.6734 (5), 9.8044 (8), 10.5156 (7)
α, β, γ (°)	65.804 (5), 89.894 (6), 74.736 (5)
V (Å^3)	601.03 (8)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.29 × 0.21 × 0.06
Data collection	
Diffractometer	Rigaku R-AXIS RAPID
Absorption correction	Multi-scan (*ABSCOR*; Higashi, 1995)
T_{min}, T_{max}	0.506, 0.995
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5815, 2739, 2065
R_{int}	0.030
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.058, 0.164, 1.10
No. of reflections	2739
No. of parameters	146
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.48, −0.26

Computer programs: *RAPID-AUTO* (Rigaku, 2010), *SHELXT2014/5* (Sheldrick, 2015*a*), *SHELXL2019/2* (Sheldrick, 2015*b*) and *DIAMOND* (Brandenburg & Putz, 1999).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2022). **7**, x221080 [https://doi.org/10.1107/S241431462201080X]

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Diethyl 4,4′-[octane-1,8-diylbis(oxy)]dibenzoate

Crystal data

$C_{26}H_{34}O_6$
M_r = 442.53
Triclinic, $P\overline{1}$
a = 6.6734 (5) Å
b = 9.8044 (8) Å
c = 10.5156 (7) Å
α = 65.804 (5)°
β = 89.894 (6)°
γ = 74.736 (5)°
V = 601.03 (8) Å^3
Z = 1
$F(000)$ = 238
D_x = 1.223 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 4497 reflections
θ = 2.4–25.9°
μ = 0.09 mm^{-1}
T = 173 K
Plate, colorless
0.29 × 0.21 × 0.06 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Detector resolution: 10.000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
T_{min} = 0.506, T_{max} = 0.995
5815 measured reflections
2739 independent reflections
2065 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 27.5°, θ_{min} = 2.1°
h = −8→8
k = −12→12
l = −13→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.164
S = 1.10
2739 reflections
146 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0845P)^2 + 0.0881P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.50078 (18)	0.61698 (14)	0.26687 (11)	0.0379 (3)
O2	−0.15521 (19)	0.27118 (15)	0.20288 (12)	0.0448 (4)
O3	−0.13007 (18)	0.21468 (14)	0.43290 (12)	0.0373 (3)
C1	0.9557 (3)	0.95272 (19)	0.06471 (16)	0.0340 (4)
H1A	0.875445	1.023516	0.104138	0.041*
H1B	1.073077	0.875112	0.136554	0.041*
C2	0.8136 (2)	0.86753 (19)	0.03467 (16)	0.0331 (4)
H2A	0.696733	0.944785	−0.037757	0.040*
H2B	0.894056	0.795510	−0.003499	0.040*
C3	0.7246 (3)	0.77505 (19)	0.16506 (16)	0.0341 (4)
H3A	0.841692	0.697379	0.237046	0.041*
H3B	0.645698	0.847111	0.203703	0.041*
C4	0.5820 (3)	0.69140 (19)	0.13702 (16)	0.0335 (4)
H4A	0.466187	0.766566	0.062869	0.040*
H4B	0.660781	0.612463	0.105526	0.040*
C5	0.3632 (2)	0.53601 (18)	0.26868 (16)	0.0306 (4)
C6	0.3009 (3)	0.51230 (19)	0.15451 (16)	0.0338 (4)
H6	0.354087	0.554669	0.067383	0.041*
C7	0.1604 (3)	0.42621 (19)	0.16981 (17)	0.0340 (4)
H7	0.118981	0.409221	0.092424	0.041*
C8	0.0786 (2)	0.36409 (18)	0.29588 (16)	0.0301 (4)
C9	0.1424 (2)	0.38832 (19)	0.40981 (16)	0.0319 (4)
H9	0.088819	0.346062	0.496787	0.038*
C10	0.2826 (3)	0.4731 (2)	0.39638 (16)	0.0339 (4)
H10	0.324872	0.489132	0.474169	0.041*
C11	−0.0794 (2)	0.28025 (18)	0.30258 (17)	0.0328 (4)
C12	−0.2826 (3)	0.1275 (2)	0.45125 (18)	0.0373 (4)
H12A	−0.225921	0.035401	0.431134	0.045*
H12B	−0.413088	0.194284	0.387294	0.045*
C13	−0.3244 (3)	0.0773 (2)	0.60203 (19)	0.0454 (5)
H13A	−0.423756	0.015410	0.620866	0.054*
H13B	−0.383525	0.169814	0.619571	0.054*
H13C	−0.193089	0.014077	0.663841	0.054*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0408 (7)	0.0495 (7)	0.0316 (6)	−0.0276 (6)	0.0102 (5)	−0.0163 (5)
O2	0.0479 (8)	0.0588 (8)	0.0391 (7)	−0.0288 (6)	0.0045 (5)	−0.0236 (6)
O3	0.0362 (6)	0.0433 (7)	0.0389 (7)	−0.0228 (5)	0.0073 (5)	−0.0170 (5)
C1	0.0341 (9)	0.0348 (8)	0.0357 (9)	−0.0156 (7)	0.0060 (7)	−0.0141 (7)
C2	0.0322 (8)	0.0345 (8)	0.0354 (9)	−0.0159 (7)	0.0063 (6)	−0.0136 (7)
C3	0.0339 (9)	0.0361 (9)	0.0342 (9)	−0.0152 (7)	0.0060 (6)	−0.0137 (7)
C4	0.0327 (8)	0.0369 (9)	0.0330 (9)	−0.0176 (7)	0.0081 (6)	−0.0123 (7)
C5	0.0274 (8)	0.0324 (8)	0.0323 (8)	−0.0106 (6)	0.0023 (6)	−0.0128 (6)

C6	0.0358 (9)	0.0394 (9)	0.0280 (8)	−0.0151 (7)	0.0074 (6)	−0.0135 (7)
C7	0.0330 (9)	0.0394 (9)	0.0334 (9)	−0.0123 (7)	0.0022 (6)	−0.0181 (7)
C8	0.0273 (8)	0.0303 (8)	0.0335 (9)	−0.0096 (6)	0.0021 (6)	−0.0134 (6)
C9	0.0309 (8)	0.0377 (9)	0.0291 (8)	−0.0146 (7)	0.0061 (6)	−0.0131 (6)
C10	0.0331 (8)	0.0438 (9)	0.0300 (8)	−0.0167 (7)	0.0038 (6)	−0.0171 (7)
C11	0.0297 (8)	0.0322 (8)	0.0380 (9)	−0.0095 (7)	0.0039 (6)	−0.0159 (7)
C12	0.0331 (9)	0.0388 (9)	0.0466 (10)	−0.0186 (7)	0.0071 (7)	−0.0196 (7)
C13	0.0458 (11)	0.0490 (11)	0.0504 (11)	−0.0260 (9)	0.0160 (8)	−0.0223 (8)

Geometric parameters (Å, º)

O1—C5	1.3581 (18)	C5—C6	1.396 (2)
O1—C4	1.4421 (18)	C5—C10	1.402 (2)
O2—C11	1.2105 (19)	C6—C7	1.386 (2)
O3—C11	1.3403 (19)	C6—H6	0.9500
O3—C12	1.4581 (18)	C7—C8	1.392 (2)
C1—C1^{i}	1.520 (3)	C7—H7	0.9500
C1—C2	1.527 (2)	C8—C9	1.400 (2)
C1—H1A	0.9900	C8—C11	1.484 (2)
C1—H1B	0.9900	C9—C10	1.378 (2)
C2—C3	1.522 (2)	C9—H9	0.9500
C2—H2A	0.9900	C10—H10	0.9500
C2—H2B	0.9900	C12—C13	1.505 (2)
C3—C4	1.508 (2)	C12—H12A	0.9900
C3—H3A	0.9900	C12—H12B	0.9900
C3—H3B	0.9900	C13—H13A	0.9800
C4—H4A	0.9900	C13—H13B	0.9800
C4—H4B	0.9900	C13—H13C	0.9800
C5—O1—C4	118.70 (12)	C7—C6—H6	120.4
C11—O3—C12	116.54 (12)	C5—C6—H6	120.4
C1^{i}—C1—C2	113.30 (16)	C6—C7—C8	121.54 (14)
C1^{i}—C1—H1A	108.9	C6—C7—H7	119.2
C2—C1—H1A	108.9	C8—C7—H7	119.2
C1^{i}—C1—H1B	108.9	C7—C8—C9	118.79 (14)
C2—C1—H1B	108.9	C7—C8—C11	118.64 (14)
H1A—C1—H1B	107.7	C9—C8—C11	122.51 (14)
C3—C2—C1	112.54 (13)	C10—C9—C8	120.34 (14)
C3—C2—H2A	109.1	C10—C9—H9	119.8
C1—C2—H2A	109.1	C8—C9—H9	119.8
C3—C2—H2B	109.1	C9—C10—C5	120.44 (14)
C1—C2—H2B	109.1	C9—C10—H10	119.8
H2A—C2—H2B	107.8	C5—C10—H10	119.8
C4—C3—C2	113.26 (13)	O2—C11—O3	123.23 (15)
C4—C3—H3A	108.9	O2—C11—C8	124.60 (15)
C2—C3—H3A	108.9	O3—C11—C8	112.17 (13)
C4—C3—H3B	108.9	O3—C12—C13	106.08 (14)
C2—C3—H3B	108.9	O3—C12—H12A	110.5

H3A—C3—H3B	107.7	C13—C12—H12A	110.5
O1—C4—C3	107.07 (12)	O3—C12—H12B	110.5
O1—C4—H4A	110.3	C13—C12—H12B	110.5
C3—C4—H4A	110.3	H12A—C12—H12B	108.7
O1—C4—H4B	110.3	C12—C13—H13A	109.5
C3—C4—H4B	110.3	C12—C13—H13B	109.5
H4A—C4—H4B	108.6	H13A—C13—H13B	109.5
O1—C5—C6	124.62 (14)	C12—C13—H13C	109.5
O1—C5—C10	115.71 (13)	H13A—C13—H13C	109.5
C6—C5—C10	119.67 (14)	H13B—C13—H13C	109.5
C7—C6—C5	119.21 (14)		

C1^{i}—C1—C2—C3	−179.35 (16)	C11—C8—C9—C10	−177.00 (15)
C1—C2—C3—C4	179.44 (14)	C8—C9—C10—C5	−0.1 (2)
C5—O1—C4—C3	178.54 (13)	O1—C5—C10—C9	−179.73 (14)
C2—C3—C4—O1	−176.76 (13)	C6—C5—C10—C9	0.0 (2)
C4—O1—C5—C6	3.3 (2)	C12—O3—C11—O2	0.8 (2)
C4—O1—C5—C10	−176.98 (13)	C12—O3—C11—C8	−179.24 (13)
O1—C5—C6—C7	179.46 (15)	C7—C8—C11—O2	−5.7 (2)
C10—C5—C6—C7	−0.2 (2)	C9—C8—C11—O2	171.73 (16)
C5—C6—C7—C8	0.6 (2)	C7—C8—C11—O3	174.33 (13)
C6—C7—C8—C9	−0.7 (2)	C9—C8—C11—O3	−8.2 (2)
C6—C7—C8—C11	176.84 (14)	C11—O3—C12—C13	−175.71 (14)
C7—C8—C9—C10	0.4 (2)		

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

Hydrogen-bond geometry (Å, º)

*Cg*1 is the centroid of the C5–C10 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3*A*···*Cg*1^{ii}	0.99	2.89	3.728 (2)	143
C12—H12*B*···*Cg*1^{iii}	0.99	2.82	3.744 (2)	155

Symmetry codes: (ii) *x*+1, *y*, *z*; (iii) *x*−1, *y*, *z*.