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Crystal structure of 1,2-[4-butoxybenzoyloxy-4′-pentyl]diphenylethane

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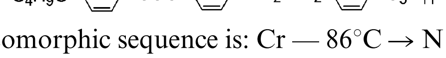
The crystal structure of 1,2-[4-butoxybenzoyloxy-4′-pentyl]diphenylethane ($C_{30}H_{36}O_3$) has been determined by direct methods using single crystal X-ray diffraction data. It crystallizes in the monoclinic system with space group $P2_1/a$ and Z=4. The unit cell parameters are: a=8.098(1), b=10.926(1), c=29.643(2) Å and β=94.01(1)°. The final reliability factor is R=0.073 and the goodness of fit is equal to 1.027. The molecular arrangement is very typical, with molecules associated in dimers very closely parallel to the Oz axis. In a given dimer, the backbones of the two molecules run alongside each other; this association can be attributed to strong dipole–dipole interactions through the polar ester and ether groups. In addition these dimers are connected to neighbours via dipole–dipole interactions along the Oy direction. There are numerous very weak van der Waals interactions, particularly between the terminal aliphatic chains.

1. Introduction

Over the last decade several crystal structures of nematogenic compounds have been published. However, the authors did not emphasize the contribution played by polar groups (ether and ester) on the molecular arrangement in the crystals. It has generally been observed that in mesogenic compounds, a knowledge of the molecular geometry and packing of the molecules in the crystalline state often helps in explaining the observed mesomorphic phase behaviour, which depends on a subtle balance between intermolecular interactions. In this case, the molecules are arranged in a parallel or antiparallel fashion according to the interactions between their polar groups (most often ether and ester) in order to maximize the overlap between neighbouring central cores. Three possible arrangements have been proposed [1–3] to describe the core fragments inserted between the ether and ester group.

In an attempt to further our understanding in this area we have 1,2-[4-butoxybenzoyloxy-4′-pentyl] diphenylethane which determined the crystal structure of exhibits a nematic phase:



The mesomorphic sequence is: Cr — 86°C → N – 138°C → I.

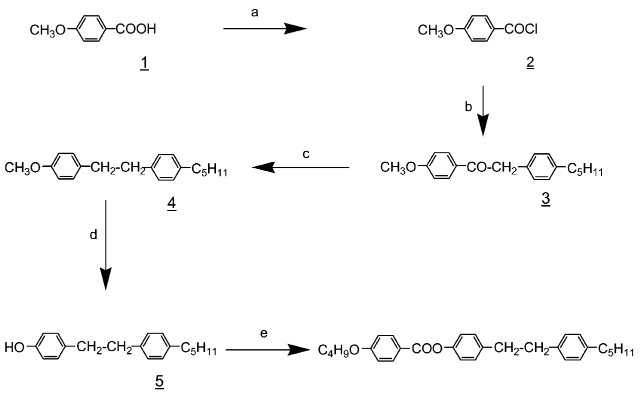
2. Experimental

2.1. *Synthesis*

The title compound was prepared using the scheme:

2.2. *X-ray diffraction, structure determination and refinement*

Transparent prismatic crystals were grown by slow evaporation of ethanol/chloroform solutions. The crystal used for the data collection has the dimensions: $0.45 \times 0.28 \times 0.05\,mm^3$. 1,2-[4-Butoxybenzoyloxy-4′-pentyl]diphenylethane, $C_{30}H_{36}O_3$, M_x=444.6 g mol^{-1},



Scheme. a) $SOCl_2$; b) C_5H_{11}-Ph, $AlCl_3$, CH_2Cl_2; c) hydrazine, KOH, diethylene glycol; d) pyridine,HCl; e) 4-butoxybenzoic acid, DCC, DMAP, CH_2Cl_2.

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crystallizes in the monoclinic system, space group $P2_1/a$ ($Z=4$). The unit cell parameters were obtained by a least-squares fit of the setting angles of 25 reflections with θ between 31° and 43°, and are: $a=8.098(1)$ $b=10.926(1)$ $c=29.643(2)$ Å and $\beta=94.01(1)°$, with a cell volume of 2616.4(4) Å^3. The calculated density, of 1.129 g cm^{-3}, is very low, as is the case for most mesogenic compounds. The linear absorption coefficient is $\mu=0.555$ mm^{-1} for CuK_α radiation (1.54178 Å) at room temperature (298 K).

The diffracted intensities were collected using a CAD-4 Enraf-Nonius diffractometer equipped with a graphite monochromator up to $\theta_{max}=70°$: $-9 \leqslant h \leqslant 9$, $0 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 36$. Three standard reflections were used to monitor the data collection and detect any decrease of intensity; the transmission factor $T(h\,k\,l)$ lies between 0.788 and 0.973; the crystal absorption correction was performed using the Ψ scan technique [4]. There were 2 797 independent reflections of which 1 508 were considered observed ($I>2\sigma(I)$) and $R_{int}=0.023$. The crystal structure was solved and refined with the SHELX97 program [5]. Scattering factors were taken from the International Tables for Crystallography [6]. The hydrogen atoms were introduced at their theoretical positions and allowed to ride with the atoms to which they are attached; the refinement was then resumed. The final reliability factor is $R=0.073$, and the goodness of fit is 1.027. The weight was $w=1/[\sigma^2(F_o^2)+(0.1581P)^2+0.4021P]$ where $P=(F_o^2+2F_c^2)/3$. The minimum and maximum residual electron densities were -0.28 and 0.24 e Å^{-3}, respectively. Important crystallographic data and refinement parameters are given in table 1.

Table 1. Crystal data and structure refinement.

Empirical formula	$C_{30}\,H_{36}\,O_3$
Formula weight (g mol^{-1})	444.59
Temperature (K)	296(2)
Wavelength (Å)	1.54180
Crystal system	monoclinic
Space group	$P21/a$ (No. 14)
Unit cell dimensions:	$a=8.098(1)$, $b=10.926(1)$, $c=29.643(2)$ Å $\alpha=90$, $\beta=94.01(1)$, $\gamma=90°$
Volume (Å^3)	2616.4(4)
N° of mol. per unit cell (Z)	4
Calculated density (g cm^{-3})	1.129
Absorption coefficient (mm^{-1})	0.555
$F(0\,0\,0)$	960
Crystal size (mm^3)	0.45 × 0.28 × 0.05
h_{min}/h_{max}, k_{min}/k_{max}, l_{min}/l_{max}	−9/9, 0/13, 0/36
Total uniquedata	2712 [R(int)=0.023]
Observed data	1508
Theta min/max (°)	1.5/70.1
Max./min. transmission	0.9728/0.7882
Refinement method	Full-matrix least-squares on F^2
N. parameters	299
Goodness-of-fit on F^2	1.027
Final R indices [$I>2\sigma(I)$]	$R_1=0.0730$, $wR_2=0.2066$
Extinction coefficient	0.0027
($\Delta\rho$)min/max (e Å^{-3})	−0.28/0.24

The crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with the no. CCDC 264143. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. *Crystal structure*

The fractional x, y, z atomic coordinates and the equivalent U_{eq} thermal motion factors are listed in table 2. The U_{eq} values for the carbon atoms at the end

Table 2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) of the non-hydrogen atoms with their standard deviations in parentheses.

Atom	x/a	y/b	z/c	U_{eq}
C2	0.6046(8)	0.1914(4)	0.44645(18)	0.064(2)
C3	0.5719(8)	0.2023(4)	0.49145(18)	0.063(2)
C4	0.6439(7)	0.1254(3)	0.52403(18)	0.0553(18)
C5	0.7477(7)	0.0330(3)	0.51087(18)	0.058(2)
C6	0.7817(7)	0.0196(4)	0.46605(18)	0.0587(18)
C7	0.6102(8)	0.1468(4)	0.5713(2)	0.062(2)
O8	0.5182(5)	0.2254(3)	0.58347(12)	0.0844(16)
O9	0.6943(5)	0.0703(3)	0.60029(12)	0.0649(16)
C10	0.6877(8)	0.0945(4)	0.64701(18)	0.059(2)
C11	0.7784(8)	0.1868(4)	0.6666(2)	0.070(2)
C12	0.7784(9)	0.2050(4)	0.7133(2)	0.071(2)
C13	0.6833(8)	0.1305(4)	0.73927(19)	0.063(2)
C14	0.5928(8)	0.0381(4)	0.7179(2)	0.075(2)
C15	0.5920(8)	0.0188(4)	0.67161(19)	0.066(2)
C16	0.6853(10)	0.1483(5)	0.7894(2)	0.083(3)
C17	0.8221(10)	0.0772(6)	0.8153(2)	0.089(3)
C20	0.8253(10)	0.0962(5)	0.8656(2)	0.086(3)
C21	0.8943(12)	0.1963(6)	0.8868(2)	0.105(4)
C22	0.8939(14)	0.2147(6)	0.9329(3)	0.112(5)
C23	0.8199(14)	0.1349(7)	0.9593(3)	0.113(4)
C24	0.7421(13)	0.0329(7)	0.9388(3)	0.109(4)
C25	0.7524(12)	0.0108(6)	0.8934(2)	0.099(4)
C31	0.823(2)	0.1672(8)	1.0096(3)	0.166(7)
C32	0.7640(16)	0.0763(7)	1.0407(2)	0.173(7)
C33	0.7623(19)	0.1300(9)	1.0877(3)	0.178(8)
C34	0.719(2)	0.0384(11)	1.1213(4)	0.218(9)
C35	0.710(2)	0.0969(13)	1.1677(3)	0.238(9)
O36	0.7466(5)	0.1012(3)	0.38963(12)	0.0648(13)
C37	0.8601(8)	0.0106(4)	0.37431(19)	0.074(2)
C38	0.8859(9)	0.0424(4)	0.32535(19)	0.074(2)
C39	0.9778(9)	0.1599(4)	0.3203(2)	0.082(2)
C40	1.0178(10)	0.1889(5)	0.2726(2)	0.105(3)

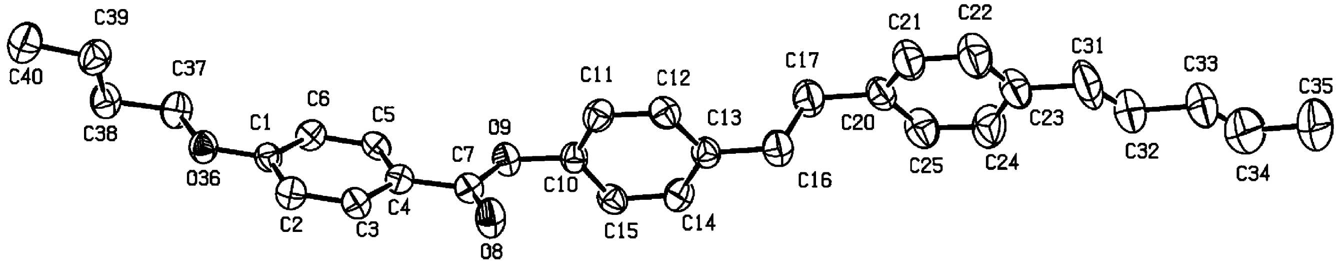

Figure 1. Ellipsoid representation (probability 30%) and atom labelling.

of the pentyl terminal chain are rather high, which is not the case for those of the butyloxy terminal chain.

The molecular conformation, the atomic labelling and the ellipsoid representation of non-hydrogen atoms is presented in figure 1 [7]. The bond lengths and bond angles together with their standard deviations are given in tables 3 and 4, respectively, and agree quite well with the literature.

The maximum and minimum bond lengths in the average aromatic phenyl rings are, respectively, 1.34(1) and 1.40(1) Å. The average observed bond angle in each of the three phenyl rings is, respectively, 116.3(4)° and 122.9(4)°. The total length of the molecule (atoms C35 to C40), the lengths of the polyaromatic core (atoms C31 to O36), of the butyloxy terminal chain (atoms O36 to C40), of the pentyl terminal chain (atoms C31 to C35) are 26.844(6), 18.358(6), 4.341(4) and 4.900(8) Å, respectively. The polar moiety (atoms O9 to O36) and the non-polar group (atoms C10 to C35) have lengths 6.296(6) and 15.370(6) Å, respectively. The molecular conformation is entirely defined by the torsion angles listed in table 5. The molecule is fully extended.

Table 3. Bond lengths (Å) for the non-hydrogen atoms with their standard deviations in parentheses.

Bond	Length	Bond	Length
C(1)–O(36)	1.369(6)	C(16)–C(17)	1.517(10)
C(1)–C(6)	1.372(7)	C(17)–C(20)	1.504(8)
C(1)–C(2)	1.400(8)	C(20)–C(21)	1.362(9)
C(2)–C(3)	1.383(8)	C(20)–C(25)	1.402(10)
C(3)–C(4)	1.378(7)	C(21)–C(22)	1.381(11)
C(4)–C(5)	1.387(6)	C(22)–C(23)	1.341(13)
C(4)–C(7)	1.465(8)	C(23)–C(24)	1.398(12)
C(5)–C(6)	1.383(8)	C(23)–C(31)	1.531(13)
C(7)–O(8)	1.208(7)	C(24)–C(25)	1.376(11)
C(7)–O(9)	1.349(7)	C(31)–C(32)	1.458(13)
O(9)–C(10)	1.415(6)	C(32)–C(33)	1.513(11)
C(10)–C(11)	1.354(7)	C(33)–C(34)	1.472(16)
C(10)–C(15)	1.377(8)	C(34)–C(35)	1.523(16)
C(11)–C(12)	1.399(8)	O(36)–C(37)	1.445(7)
C(12)–C(13)	1.390(8)	C(37)–C(38)	1.521(8)
C(13)–C(14)	1.376(7)	C(38)–C(39)	1.497(7)
C(13)–C(16)	1.498(8)	C(39)–C(40)	1.506(9)
C(14)–C(15)	1.388(8)		

The phenyl rings $\varnothing_1$ (atoms C1 to C6), $\varnothing_2$ (atoms C10 to C15) and $\varnothing_3$(C20 to C25) are planar with the dihedral angles: $\varnothing_2/\varnothing_1=77.0(2)^\circ$ and $\varnothing_3/\varnothing_2=8.8(3)^\circ$. Moreover the benzoate group (atoms C1 to O9) is planar, as generally observed in the literature.

In all dimers there are dipole–dipole interactions between: (1) the neighbouring carboxylate groups of

Table 4. Bond angles (°) for the non-hydrogen atoms with their standard deviations in parentheses.

Bond angle	Value	Bond angle	Value
O(36)–C(1)–C(6)	125.1(5)	C(13)–C(14)–C(15)	122.2(5)
O(36)–C(1)–C(2)	114.2(4)	C(10)–C(15)–C(14)	117.9(5)
C(2)–C(1)–C(6)	120.7(5)	C(17)–C(16)–C(13)	113.1(5)
C(1)–C(2)–C(3)	118.4(5)	C(16)–C(17)–C(20)	113.1(6)
C(2)–C(3)–C(4)	121.5(5)	C(21)–C(20)–C(25)	116.1(6)
C(3)–C(4)–C(5)	118.8(5)	C(21)–C(20)–C(17)	123.1(6)
C(3)–C(4)–C(7)	118.4(4)	C(25)–C(20)–C(17)	120.8(6)
C(5)–C(4)–C(7)	122.8(5)	C(20)–C(21)–C(22)	123.0(7)
C(4)–C(5)–C(6)	120.8(4)	C(21)–C(22)–C(23)	121.0(8)
C(1)–C(6)–C(5)	119.6(5)	C(22)–C(23)–C(24)	118.1(8)
O(8)–C(7)–O(9)	123.0(5)	C(22)–C(23)–C(31)	116.2(8)
O(8)–C(7)–C(4)	124.0(5)	C(24)–C(23)–C(31)	125.7(9)
O(9)–C(7)–C(4)	113.0(4)	C(23)–C(24)–C(25)	120.6(8)
C(7)–O(9)–C(10)	117.1(4)	C(20)–C(25)–C(24)	121.0(6)
C(11)–C(10)–C(15)	121.9(5)	C(23)–C(31)–C(32)	118.4(8)
C(11)–C(10)–O(9)	120.2(5)	C(31)–C(32)–C(33)	110.0(7)
C(15)–C(10)–O(9)	117.9(4)	C(32)–C(33)–C(34)	112.2(8)
C(10)–C(11)–C(12)	119.5(5)	C(33)–C(34)–C(35)	110.8(10)
C(13)–C(12)–C(11)	120.2(5)	C(1)–O(36)–C(37)	117.8(4)
C(14)–C(13)–C(12)	118.2(5)	O(36)–C(37)–C(38)	106.0(4)
C(14)–C(13)–C(16)	121.4(5)	C(37)–C(38)–C(39)	113.2(5)
C(12)–C(13)–C(16)	120.4(5)	C(38)–C(39)–C(40)	114.5(5)

Table 5. Significant torsion angles (°) with their standard deviations in parentheses.

C2–C1–O36–C37	*trans*[a]	C22–C23–C31–C32	*trans*
C3–C4–C7–O9	*trans*	C23–C31–C32–C33	*trans*
C4–C7–O9–C10	*trans*	C31–C32–C33–C34	*trans*
C7–O9–C10–C11	−76.3(7)	C32–C33–C34–C35	*trans*
C12–C13–C16–C17	−87.7(7)	C1–O36–C37–C38	*trans*
C13–C16–C17–C20	*trans*	O36–C37–C38–C39	67.8(7)
C16–C17–C20–C21	−80.2(10)	C37–C38–C39–C40	*trans*

[a] Differing by less than 10° from 180°.

both molecules (mode I) [1, 2]; (2) the neighbouring ether groups of both molecules (mode III) [2, 3].

Within a single dimer, both molecules are oriented in the same direction, pratically aligned along the *c*-axis (within 3°), so that there is a maximum overlap through van der Waals interactions, reinforcing the dipole–dipole interactions.

In a dimer pair of molecules, the shortest O … O distances between (1) two adjacent carboxylate groups (mode I) [1] are *d*[(O8, I) … (O8, II)]=4.085(6) Å, *d*[(O9, I) … (O8, II)]=3.506(5) Å; and (2) between two adjacent ether groups (mode III) [2], *d*[(O36, I) … (O36, II)]=5.193(5) Å, where I=(x, y, z) and II=($1/2+x$, $1/2-y$, z) as an example.

Between neighbouring dimers, there are also dipole–dipole interactions involving one ester and one ether group (mode II) [1]. The shortest O … O distances are *d*[(O8, III) … (O36, IV)]=4.267(6) Å and *d*[(O9, III) … (O36, IV)]=4.062(5) Å.

In addition there are numerous weak van der Waals interactions between the pentyl terminal groups. The molecular projections on the (xOz) and the (yOz) planes are shown in figures 2 and 3.

In the crystal, neighbouring dimers are arranged head-to-tail so that the global dipole moment is zero. As has already been stressed, the molecular arrangement is greatly dependent on the relative position of the dipolar groups, which play the leading role in determining the molecular packing of the molecules. Strickly, the molecular arrangement is nematic-like (all molecules approximately aligned about one direction, here the *c*-axis) but with a tendency towards smectic-like, e.g. with a layer-ordering tendency perpendicular to that direction.

3.2. *Molecular modelling*

Preliminary molecular modelling calculations using the software Hyperchem 7.5 for windows [8] have been carried out using the semi-empirical PM3 method. A single point calculation on an isolated molecule as extracted from the crystal yields a dipolar moment of 2.81 D. The latter is not parallel to the molecular

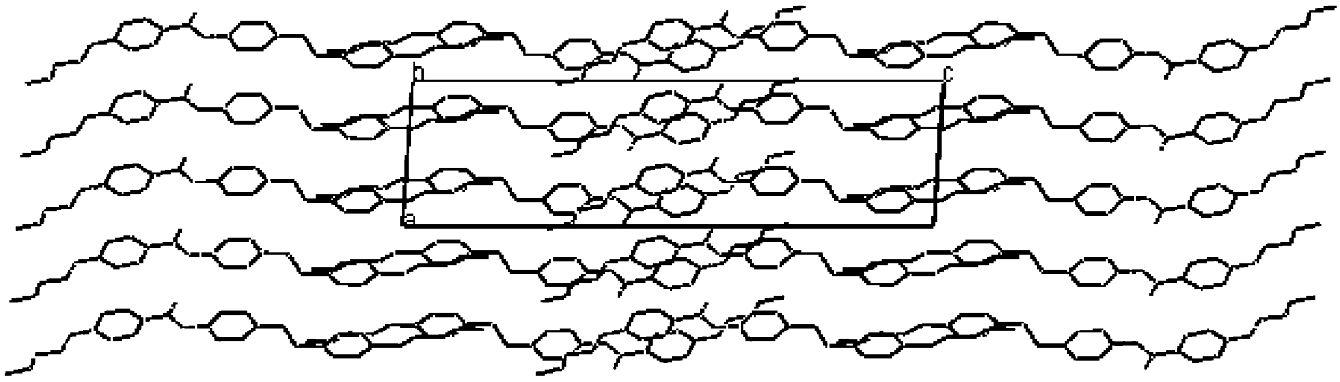

Figure 2. Crystal structure; view along the *b*-axis.

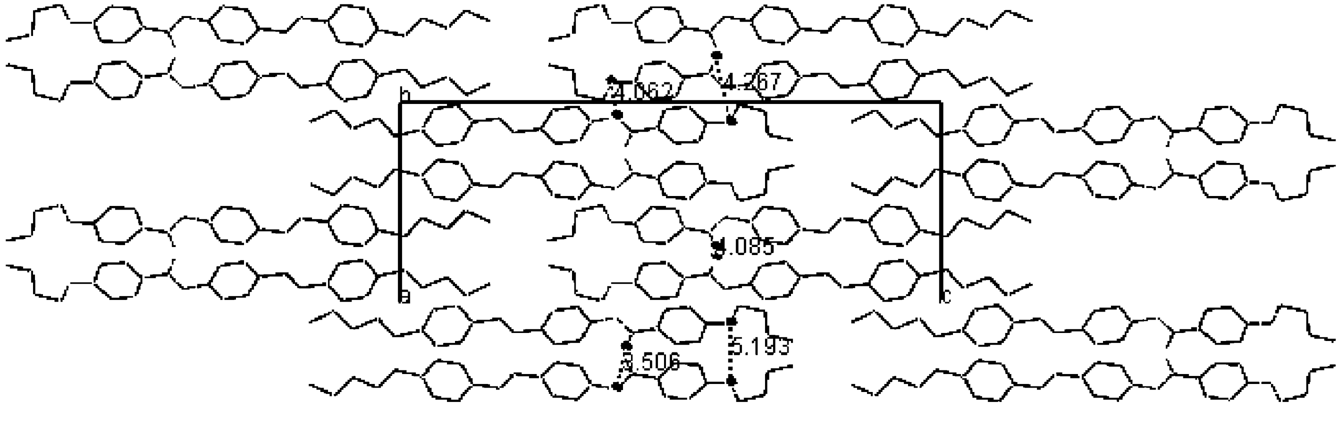

Figure 3. Crystal structure; view along the *a*-axis.

backbone. Optimizing the geometry of the molecule as if *in vacuo* resulted in a slightly modified conformation but produced a similar value for the dipolar moment (2.89 D) and confirmed an orientation markedly distinct from that of the molecular backbone.

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