

4'-[2-(2-Ethoxyethoxy)ethoxy]biphenyl-4-carboxylic acid: correlation between its crystalline and smectic phases

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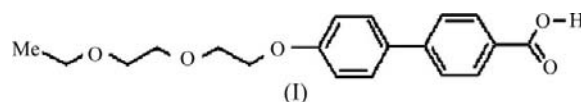
The crystal structure of the dimeric title compound, C₁₉H₂₂O₅, is dominated by a head-to-head hydrogen-bonding interaction between centrosymmetrically related carboxyl groups in each monomer. The result is a dimeric axis of unusual length (*ca* 34 Å), but still shorter than what could be expected for a fully extended chain, owing to two turning points in the oligoethoxy ends. This allows for an explanation of the structure of the smectic mesophase exhibited by this compound and at the same time fully validates former geometric estimations based on PM3 calculations.

Comment

The smectic C (SmC) mesophase is one of the oldest and best studied types of liquid crystals (LCs), from both the experimental and the theoretical points of view (Goodby, 1998). Most of these studies were conducted with the aim of understanding at the molecular level the distinctive structural features of the SmC mesophase: a lamellar arrangement of elongated molecules, tilted on average by an angle θ from the normal to the lamellae. Several techniques have been used in order to assess specific aspects of the intermolecular organization in a wide variety of SmC materials, and different theoretical approaches have been followed in order to either describe the phase transitions between the SmC, SmA and nematic (N) phases (Guillon, 1998; Huang, 1998) or suggest suitable models for the tilted lamellar organization, either in compounds with dipolar moments noncollinear with the main molecular axis or in compounds without any dipolar moment but containing molecular fragments with different lateral

areas, giving rise to different packing requirements. In spite of the amount of time devoted to their study, interest in SmC LCs is still alive (Sanchez Ferrer & Finkelmann, 2008; Vadnais *et al.*, 2008), owing to the applications they exhibit, for example, in electro-optic devices, such as surface stabilized ferroelectric liquid crystal displays (Shinkawa *et al.*, 2008; Wang & Bos, 2004).

As part of a systematic study (Montani *et al.*, 2009) with calamitic (*i.e.* rod-shaped) mesogens of three-block molecular architecture (biphenyl, aliphatic chains, oxyethylene chains), the LC behaviour of 4'-[2-(2-ethoxyethoxy)ethoxy]biphenyl-4-carboxylic acid, (I), has been studied. This compound can be *a priori* considered as a calamitic mesogen consisting of dimeric units formed by hydrogen-bonding association of the carboxyl groups. In such a case, the central core would have five rings, and there would be two terminal oxyethylene chains, a molecular geometry suitable for smectic mesophases.



As shown by polarized optical microscopy and powder X-ray diffraction (Montani *et al.*, 2009), (I) did exhibit an SmC mesophase from 458 to 463 K, with an interlamellar distance of 30.8 Å. This value cannot be simply explained in terms of tilted extended molecules; indeed, the PM3-estimated (Stewart, 1988) molecular length for a fully extended dimer of (I) is 45 Å, significantly longer than the interlamellar distance. Even if a tilt of *ca* 45° could account for this difference, this value looks unacceptable, as the extreme tilt angles already found in SmC phases are 38°. A *gauche* conformation for the oxyethylene chains of the dimeric unit thus seems a more realistic explanation; indeed, this hypothesis finds two additional *a priori* supports: (i) the PM3-calculated molecular length for this conformation (35 Å) is much closer to the experimental interlamellar distance, and (ii) a search of the Cambridge Structural Database (CSD; Allen, 2002) for compounds with oxyethylene chains whose conformation is not determined by specific interactions (like cation complexation) showed *anti* conformations in less than 25% of cases.

As a key step in validating this hypothesis, we have succeeded in crystallizing and solving the crystalline structure of (I), shown in Fig. 1. The figure also depicts the head-to-head hydrogen-bonding interaction between the centrosymmetrically related carboxyl groups (Table 1); this rather strong interaction leads to the formation of the expected extended dimeric units, with a span of *ca* 34 Å between the outermost methyl groups. The interatomic bond distances and angles are unexceptional, save perhaps for an apparent shortening in bond lengths while traversing the chain towards the ethyl end, ascribable to libration and tied to the increasing vibration of the tail (see *Experimental*). The main conformational aspects of the molecules are to be found in the few torsion angles differing significantly (by more than 5°) from 0 or 180°, *viz.*

C5—C6—C7—C8 of $15.1(3)^\circ$, O13—C14—C15—O16 of $-72.1(3)^\circ$ and O16—C17—C18—O19 of $72.2(3)^\circ$. The first angle accounts for the slight rotation of the two benzene rings, while the remaining two represent a twofold bending of the dimer's linear 'spine' defined by the O13...O13ⁱ [symmetry code: (i) $-x, -y + 1, -z + 2$] vector, 23.688(1) Å in length. This line, representative of the molecular direction, makes angles of 46.0(1), 89.3(1) and 37.8(1) $^\circ$ with the *a*, *b* and *c* crystallographic axes, respectively; thus, the dimeric axes are almost contained by the (010) plane and nearly aligned to the crystallographic [10 $\bar{3}$] direction.

The rather small rotation between benzene rings in the monomers, as well as the restraints imposed by symmetry on the related counterpart completing the dimer, force the four aromatic rings plus their carboxylate ends to stay within a rather well defined plane (the mean deviation for the 30 atoms is 0.12 Å); the terminal tails in the dimers protrude outwards in an 'anti' fashion and their least-squares lines subtend to the plane normal an angle of *ca* 120 $^\circ$. The dimers are organized in pairs, with their axes approximately parallel to each other but rotated around this axis by about 65(1) $^\circ$, as measured by the dihedral angle between the latter least-squares planes (see Fig. 1). There is no π stacking in the structure (no coplanarity and a minimum centre-to-centre distance of 4.80 Å). The oxyethylene chains of both components of each pair mutually interdigitate (the minimum O...C distance is approximately 3.4 Å), being nearly perpendicular to the mean molecular planes, as a consequence of the *gauche* conformations exhibited around the C14—C15 and C17—C18 bonds (all other torsion angles corresponding to *trans* conformations). Fig. 2 shows two packing views along the *b* and *c* axes; the way in which the dimers align, as well as the broad two-dimensional

structure their association through weak C—H...O and C—H... π interactions (Table 1) gives rise to, can be clearly appreciated, with the hydrophobic methyl groups bunching at heights of $x \approx 0.50$ and the hydrophilic carboxylates in the vicinity of $x \approx 0.00$. Thus, the results presented here support our original hypothesis for the molecular description of the SmC phase of (I) and fully validate the geometric estimations made: in the crystalline phase, the compound exhibits a *gauche* conformation for the oxyethylene chains, with a total molecular length of 34 Å, in excellent agreement with that predicted by PM3 calculations. Moreover, a lamellar organization is still present in the crystalline phase, also showing strong microsegregation between the aromatic parts and the oxyethylene chains, probably as a consequence of their differences both in polarity and in packing requirements. Microsegregation is widely recognized as a driving force for lamellar structures (Tschierske, 1998, 2001). The interlamellar distance measured by powder X-ray diffraction in the SmC phase of (I) is close to that found in the crystalline phase, which can be taken as the crystallographic *a* parameter [30.8 *versus* 25.430(7) Å]. The difference can arise from several factors:

(i) The crystal structure has been solved at room temperature, and if an extrapolation of the molecular length to 460 K (corresponding to the SmC phase) is made, an additional 1.7 Å is obtained when only the dependence on temperature of the methylene volume (Guillon *et al.*, 1986) is taken into account. For the whole molecule, this could be estimated as 2–3 Å.

(ii) In addition, the tilt angle can vary, as stated above, from its crystallographic value (*ca* 43 $^\circ$) to *ca* 28 $^\circ$ (acceptable for SmC phases).

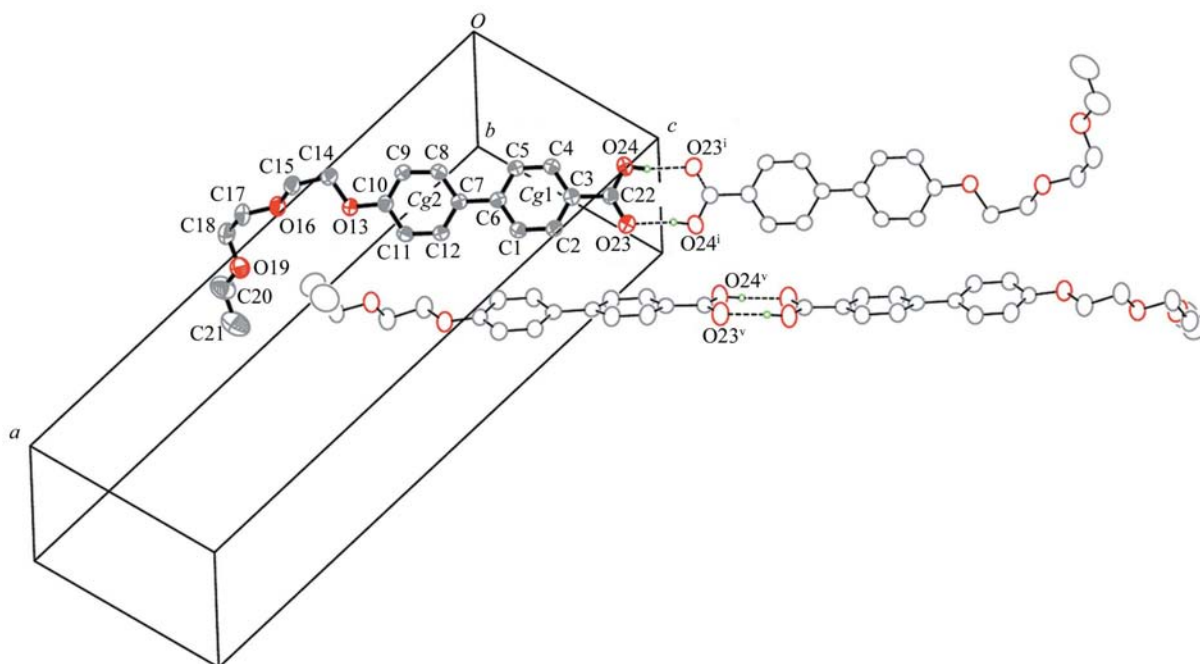


Figure 1

The hydrogen-bonded dimeric units in (I), showing the head-to-head linking of the monomers. Note the relative orientation (65 $^\circ$ apart) of the almost planar biphenyl groups in neighbouring dimers. Displacement ellipsoids are drawn at the 40% probability level. [Symmetry codes: (i) $-x, -y + 1, -z + 2$; (v) $x, -y + \frac{3}{2}, z + 1$.]

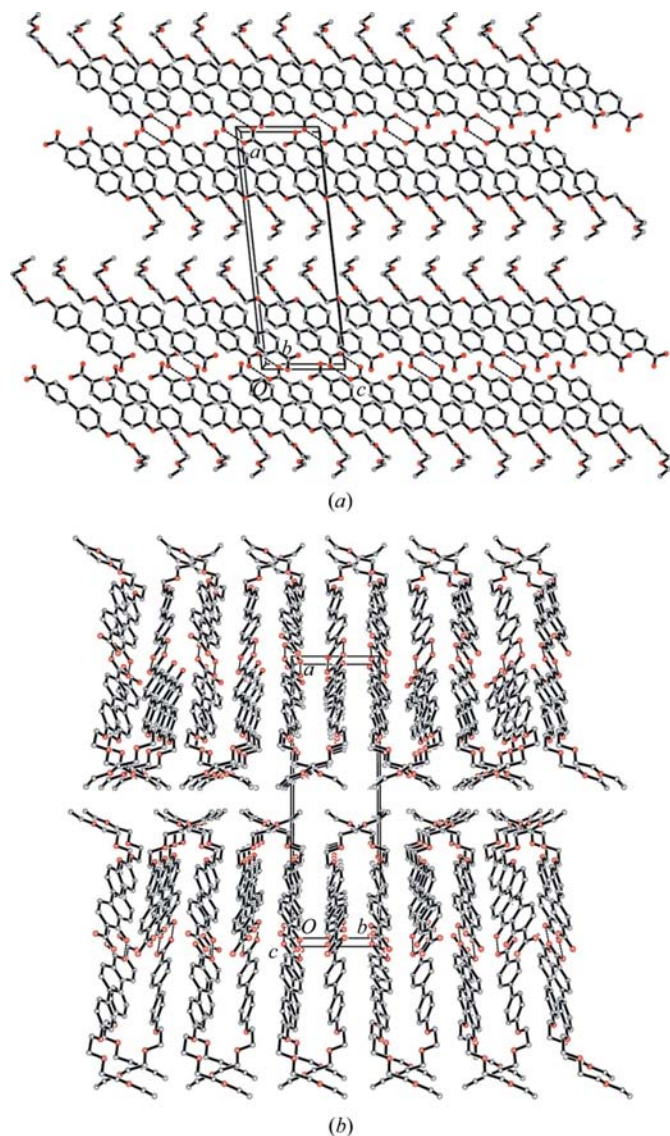


Figure 2

Projections of the structure (a) down *b* and (b) down *c*, showing two different views of the broad two-dimensional structures formed by the interlinked dimers. Note the hydrophobic methyl groups bunching at $x \simeq 0.50$ and the hydrophilic carboxylates in the vicinity of $x \simeq 0.00$.

(iii) Finally, some conformational disorder at the oxyethylene chains may appear, increasing the effective molecular length. As stated above, the oxyethylene chains point towards a direction nearly orthogonal to the mean molecular plane. The effective molecular length in the direction of the $C3 \cdots C10$ axis is *ca* 32–33 Å.

This study is an additional proof of the usefulness of single-crystal analysis for providing key information in the interpretation of LC structures at the molecular level.

Experimental

Reagents and solvents were purchased from Aldrich and were used without further purification unless otherwise specified. The reported melting points are not corrected.

Compound (I) was obtained in four consecutive steps. First, 2-(2-ethoxyethoxy)ethyl 4-methylbenzenesulfonate was prepared from 2-(2-ethoxyethoxy)ethanol (Aldrich) following a reported procedure (Lenz *et al.*, 1991). Secondly, the treatment of the tosylate with LiBr yielded the bromide (II), which was then attached to the biphenyl unit to afford the ester (III). Finally, the hydrolysis of (III) in a basic medium afforded the acid (I).

For the preparation of 2-bromo-1-(2-ethoxyethoxy)ethane, (II), LiBr (10.4 g, 0.12 mol) and 2-(2-ethoxyethoxy)ethyl 4-methylbenzenesulfonate (Lenz *et al.*, 1991) (34.4 g, 0.12 mol) in dry acetone (220 ml) were heated under reflux for 24 h under a nitrogen atmosphere. The mixture was allowed to cool to room temperature and the suspended solid was filtered off. The acetone was removed from the filtrate under reduced pressure. The remaining oil was dissolved in CH_2Cl_2 (300 ml), washed with water (2×150 ml) and dried (Na_2SO_4), and the solvent was removed under reduced pressure to afford an oil (yield 21.4 g, 91%). 1H NMR ($CDCl_3$): δ_H 3.78 (*t*, 2H, $J = 6.4$ Hz), 3.74 (*t*, 2H, $J = 6.4$ Hz), 3.66 (*t*, 2H, $J = 6.4$ Hz), 3.48 (*c*, 2H, $J = 7.06$ Hz), 3.45 (*t*, 2H, $J = 7.2$ Hz), 1.18 (*t*, 3H, $J = 7.06$ Hz).

For the preparation of methyl 4'-[2-(2-ethoxyethoxy)ethoxy]biphenyl-4-carboxylate, (III), methyl 4,4'-hydroxybiphenyl-4-carboxylate (7.5 g, 32.8 mmol) and K_2CO_3 (10.9 g, 79 mmol) were dissolved in dimethylformamide (24 ml) and heated at 373 K for an hour. A solution of (II) (10.9 g, 79 mmol) in dimethylformamide (4 ml) was then added slowly. The reaction mixture was heated under reflux for 3 d and then poured into water (150 ml), and the solid product was isolated by filtration, dried under vacuum and then recrystallized from cyclohexane to yield the methyl ester as a yellow solid (yield 9.5 g, 84%; m.p. 368 K). 1H NMR ($CDCl_3$): δ_H 8.05 (*d*, 2H, $J = 8.40$ Hz), 7.59 (*d*, 2H, $J = 8.40$ Hz), 7.53 (*d*, 2H, $J = 8.77$ Hz), 6.98 (*d*, 2H, $J = 8.78$ Hz), 4.17 (*t*, 2H, $J = 5.01$ Hz), 3.91 (*s*, 3H, $J = 5.01$ Hz), 3.87 (*t*, 2H, $J = 5.01$ Hz), 3.73 (*t*, 2H, $J = 4.95$ Hz), 3.62 (*t*, 2H, $J = 4.95$ Hz), 3.52 (*c*, 2H, $J = 7.05$ Hz), 1.20 (*t*, 3H, $J = 7.06$ Hz).

For the preparation (I), a mixture of water (2.5 ml), methanol (47.5 ml), KOH (3.3 g, 60 mmol) and methyl ester (III) (7 g, 20.3 mmol) was heated under reflux for 24 h. The solvent was then removed under reduced pressure. The residue was treated with 10 *N* HCl (15 ml) and diethyl ether (100 ml). The solid was filtered off and recrystallized from benzene, yielding the acid (I) as a white solid (yield 7.6 g, 70%; m.p. 458 K). 1H NMR ($CDCl_3$): δ_H 8.12 (*d*, 2H 2,4 , $J = 7.05$ Hz), 7.62 (*d*, 2H 1,5 , $J = 7.06$ Hz), 7.54 (*d*, 2H 8,12 , $J = 7.25$ Hz), 6.99 (*d*, 2H 9,11 , $J = 7.25$ Hz), 4.18 (*t*, 2H 14 , $J = 3.63$ Hz), 3.88 (*t*, 2H 15 , $J = 3.63$ Hz), 3.73 (*t*, 2H 17 , $J = 3.62$ Hz), 3.62 (*t*, 2H 18 , $J = 3.63$ Hz), 3.54 (*c*, 2H 20 , $J = 6.87$ Hz), 1.21 (*t*, 3H 21 , $J = 6.87$ Hz). ^{13}C NMR ($CDCl_3$): δ 170.2 (C^{22}), 156.9 (C^{10}), 142.0 (C^6), 131.1 ($C^{2,4}$), 129.5 (C^3), 128.9 ($C^{8,12}$), 128.5 (C^7), 128.2 ($C^{1,5}$), 115.5 ($C^{9,11}$), 70.6 (C^{17}), 70.3 (C^{18}), 70.1 (C^{15}), 69.8 (C^{14}), 67.7 (C^{20}), 15.4 (C^{21}). Analysis calculated for $C_{19}H_{22}O_5$: C 69.07, H 6.71%; found: C 68.90, H 6.63%.

Small plates of colourless single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a dichloromethane solution of (I) at room temperature.

Crystal data

$C_{19}H_{22}O_5$	$Z = 4$
$M_r = 330.37$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	$\mu = 0.09$ mm $^{-1}$
$a = 25.430$ (7) Å	$T = 294$ (2) K
$b = 7.769$ (2) Å	$0.60 \times 0.50 \times 0.10$ mm
$c = 8.656$ (2) Å	
$\beta = 96.187$ (5)°	
$V = 1700.3$ (8) Å 3	

Data collection

Bruker SMART CCD area-detector diffractometer 9420 measured reflections
 3634 independent reflections
 Absorption correction: multi-scan (SADABS in SAINT-NT; Bruker, 2002) 2230 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $T_{\text{min}} = 0.95$, $T_{\text{max}} = 0.99$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.063$ 219 parameters
 $wR(F^2) = 0.191$ H-atom parameters constrained
 $S = 0.99$ $\Delta\rho_{\text{max}} = 0.23 \text{ e } \text{\AA}^{-3}$
 3634 reflections $\Delta\rho_{\text{min}} = -0.14 \text{ e } \text{\AA}^{-3}$

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

Cg2 is the centroid of the C7–C12 ring.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O24–H24 \cdots O23 ⁱ	0.82	1.80	2.619 (2)	176
C18–H18B \cdots O13 ⁱⁱ	0.97	2.58	3.478 (3)	154
C1–H1 \cdots Cg2 ⁱⁱⁱ	0.93	2.83	2.83	138
C14–H14B \cdots Cg2 ^{iv}	0.97	2.74	2.74	149

Symmetry codes: (i) $-x, -y + 1, -z + 2$; (ii) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (iii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (iv) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

Atoms in the unbound $-\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OEt}$ group exhibit an increasing vibrational behaviour when traversing the tail from the phenyl-bound O atom [$U_{\text{eq}}(\text{O}) = 0.0570$ (4) \AA^2] towards the ethyl end [$U_{\text{eq}}(\text{C}) = 0.1313$ (15) \AA^2]. This is a feature found in many reported structures with similarly unbound end groups, as inspection of the CSD confirms [see, for instance, entries AABHTZ (Werner, 1976), FAZFIW (Barton *et al.*, 2004), LENLUL (McFadden *et al.*, 1994), LIXCEA (Liu *et al.*, 1999), OKARUN (Smith *et al.*, 2003) and VUMTUS (Verboom *et al.*, 1992); all of these correspond to reasonably well refined structures with $R < 0.075$ and no apparent disorder]. H atoms were placed at calculated positions [$\text{C}-\text{H} = 0.93$ (aromatic), 0.96 (methyl) or 0.97 \AA (ethyl) and $\text{O}-\text{H} = 0.82 \text{ \AA}$] and allowed to ride; in addition, methyl groups were allowed to rotate. Displacement parameters were taken as $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{carrier})$, where $x = 1.5$ for methyl H atoms or $x = 1.2$ for all other H atoms.

Data collection: SMART-NT (Bruker, 2001); cell refinement: SAINT-NT (Bruker, 2002); data reduction: SAINT-NT; 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: SHELXTL and PLATON (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3269). Services for accessing these data are described at the back of the journal.

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