



4'-(2-(2-Ethoxyethoxy)ethoxy)biphenyl-4-carboxylic acid—a polar smectogen for amphipathic liquid crystals

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ABSTRACT

We describe a new calamitic smectogen and some of its esters with a three-block molecular architecture (polar oxyethylene chain, rigid biphenyl and non-polar aliphatic chain) which were characterised by a combination of optical, thermal, X-ray and computational techniques. The title compound is a valuable smectogenic building block for amphipathic functional organic materials.

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Linear polyphilic molecules^{1,2} self-assemble in a variety of well-defined anisotropic mesophases, including lamellar liquid crystal-line phases whose occurrence led to improvements in the performance of molecular organic materials.³ In this context, the replacement in calamitic (i.e., rod shaped) mesogens of apolar methylene terminal chains by polar oxyethylene moieties leads to significant changes in their aggregation behaviour in the bulk, at surface or phase boundaries as well as in their dipole moment and ionophore activity; thus broadening their potential for applications in a wide range of fields, ranging from selectors in liquid chromatography⁴ to nanowires or anisotropic materials for electro or electro-optical devices.^{5,6} However, oligo(oxyethylene) chains usually decrease the clearing temperatures of the mesophases of small calamitic molecules and strongly perturb lamellar structures such as the smectic phases.^{1,3} This behaviour has been customarily ascribed to the tendency of oxyethylene units to adopt the preferred *gauche* conformations resulting in helical chains with larger lateral mean area per chain and shorter length than linear aliphatic chains of the same length. Nevertheless, the search for smectogenic oxyethylene-containing mesogens is of interest since they are expected to show both lamellar structures and enhanced properties. Herein we describe a new calamitic smectogen, **1a**, and some of its esters with a three-block molecular architecture (polar oxyethylene chain, rigid biphenyl and non-polar aliphatic chain) which were characterised by a combination of optical, thermal, X-ray diffraction, crystallographic and computational techniques.

The synthesis of the acid **1a** and its esters is outlined in Scheme 1. The use of the bromide instead of the parent tosylate significantly improved the synthesis of **1a** in terms of yield and ease of workup. Most of the compounds were prepared by well-known

synthetic procedures. But all attempts to obtain the dimers **5a–d** by direct esterification from the acid **1a** using DCC/DMAP as well as by condensation of the acid chloride of **1a** with the diphenol in the presence of an organic base using different conditions failed in our hands. Finally, we succeeded by employing a direct condensation which consists in the in situ treatment of the acid with a cold mixture of SOCl₂/pyridine followed by the addition of the diphenol, a procedure that has been used to obtain high-molecular weight phenolic polyesters.⁷

The liquid crystalline behaviour of **1a** was initially investigated by polarising optical microscopy (POM) and differential scanning calorimetry (DSC). Transition temperatures and associated enthalpies obtained from DSC thermograms of compound **1a** and its ester derivatives **3a–b** and **5a–b** are shown in Table 1. The DSC thermogram of **1a** shows three types of phase transition in both heating and cooling cycles with rather large enthalpy changes while the textures observed by POM confirmed that **1a** exhibits enantiotropic smectic and nematic phases. But the focal-conic fan textures observed by POM as well as the interlamellar *d*-spacing of 30.8 Å, which was measured from the powder X-ray diffraction (XRD) pattern recorded at 187 °C just before sample crystallisation, were compatible with layered structures in which the molecular long axes of the mesogens could adopt a disposition either parallel, a smectic A phase (SmA), or tilted (SmC) with respect to the normal to the layer planes.

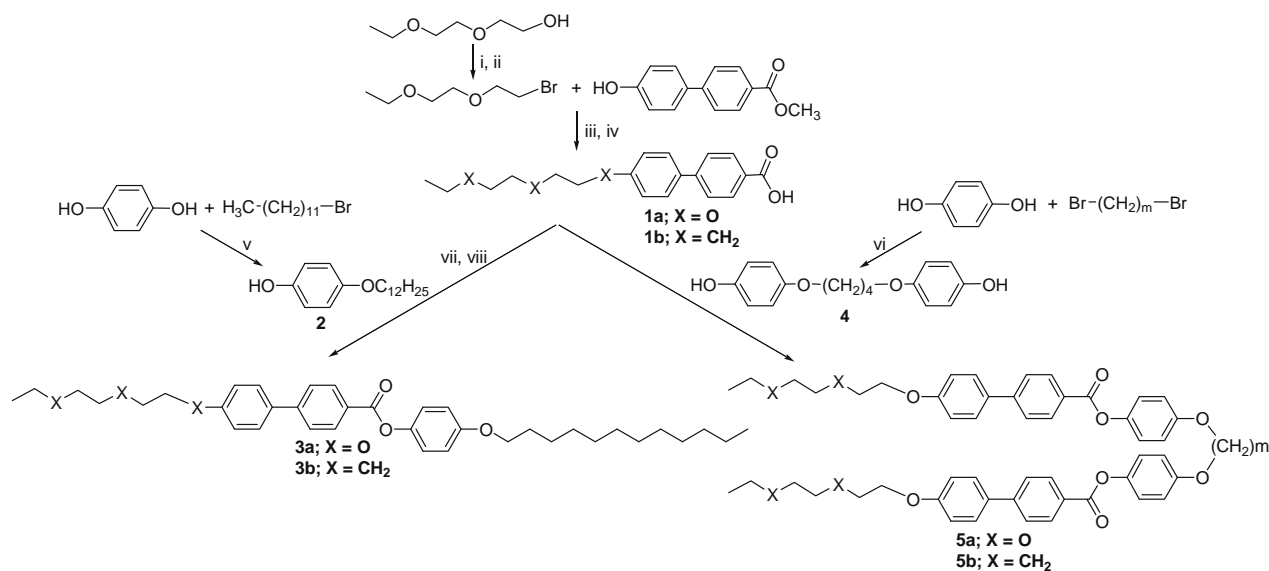
In order to shed light upon this matter, the experimental observations were complemented with theoretical calculations at the MP3 MO level. Since the acid **1a** can be considered as a dimeric calamitic mesogen formed by hydrogen-bonding association,⁸ the molecular length *L* of the dimer of **1a** was calculated with the oxyethylene tail in an all-*anti* fashion as well as with *gauche* conformations. Remarkably, the latter dimer conformation reached the global minimum without a need to restrain any geometric

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Table 1
Phase transition temperatures and enthalpies [in square brackets] for **1a** and its ester derivatives **3a–b** and **5a–b**

	Cr	Transition temperatures/°C [$\Delta H/kJ mol^{-1}$]						
		SmX	SmB	SmC	SmA	N	I	
1a	●	185[14.6]		●	190[5.35]		●	202[2.42]
3a	●	90[48.2]		●	119 ^a	●	157[5.61]	●
3b	●	67[36.1]	●	●	109[3.00]	●	185[6.90]	●
5a	●	198[81.6]	●			●	211[1.90]	●
5b	●	195[70.4]				●	251[1.60]	●

^a Transition only observed by POM.



Scheme 1. Reagents and conditions: (i) NaOH/TsCl (85%); (ii) LiBr/acetone/reflux (91%); (iii) K_2CO_3 /DMF, 100 °C (84%); (iv) KOH/MeOH–H₂O, reflux (70%); (v) K_2CO_3 /cyclohexanone, reflux (25%); (vi) $SOCl_2$, reflux; (vii) pyridine, 125 °C (84%); (viii) $SOCl_2$ –pyridine, 4 °C.

parameter, thus the calculated lengths were 45.9 Å and 35.2 Å, respectively. To explain the observed value of 30.8 Å to our point of view it seems reasonable to consider that the layer is formed by dimers with *gauche* conformations that adopt an average tilt angle of 28°.

The best evidence for this model was given by the single-crystal X-ray structure of **1a** that we described in detail in another report,⁹ which manifests two highly revealing features as can be seen in Figure 1. Firstly, it displays a smectic-type layered structure formed by dimers with head-to-head hydrogen-bonding interactions showing a strong micro-segregation between the aromatic moieties and the oxyethylene chains. Secondly, as a result of the occurrence of *gauche* conformations around the C14–C15 and the C17–C18 bonds, the terminal tails in the dimers are protruding outwards so that the effective molecular length in the crystalline phase along the direction of the dimer long axis is ca. 34 Å, in excellent agreement with that estimated from PM3 calculations. Figure 1 also shows the dimer conformation observed in the crystallographic study along with the calculated one.

The DSC thermogram of the monoester **3a** with a three-block molecular architecture (oxyethylene chain, biphenyl and aliphatic chain) only showed two distinct phase transitions in both heating and cooling cycles, corresponding to the melting and clearing transitions. POM observations showed that **3a** exhibits a SmA phase with focal conic and homeotropic textures at higher temperatures and a SmC phase with Schlieren textures at lower temperatures, with a SmA–SmC transition at about 119 °C that was not detected by DSC. This was confirmed by the X-ray patterns recorded between 105 °C and 150 °C, which are characteristic of SmA or SmC phases. They contain a very strong first-order reflection and a weak

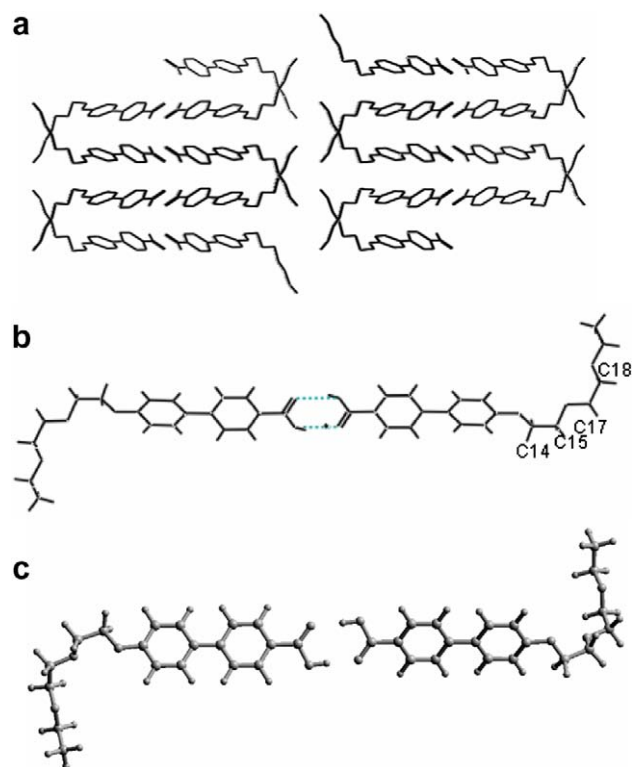


Figure 1. (a) Packing diagram of **1a** viewed down the *c* axis. (b) X-ray crystal structure. (c) PM3 gas-phase structure.

second-order reflection in the small angle region corresponding to the layer stacking in addition to a diffuse reflection in the wide region occurring from lateral distances between molecules, while the layer spacing dependence upon temperature exhibits the usual shape: an increase with temperature in the SmC phase, related to the tilt angle variation (17° at 105°C), and a very slight decrease in the SmA phase, related to the nematic order parameter decrease (Fig. 2b).

For this mesogen, a direct comparison can be made between the XRD interlamellar distance of 39.9 \AA observed at 120°C in the SmA phase and the PM3 calculated L -values. So, the molecular length L of **3a** was calculated both with the oxyethylene chain in an all-*anti* conformation and with *gauche* conformations while the methylene chain always was in an all-*anti* fashion. Accordingly, the calculated lengths were 43.7 \AA and 38.8 \AA , respectively. Again, the likeness between the experimental d -value and the calculated L -value indicates that the oxyethylene chains are in a predominantly *gauche* fashion within the SmA phase, a conclusion that can be extended on thermodynamical grounds to the lower temperature SmC phase. In addition, the calculation of the molecular coverage S of **3a** of the smectic layer¹⁰ by using the molecular volume¹¹ and the interlamellar distance gives a value for the molecular area $S = V/d$ of 24 \AA^2 , a value close to the cross-sectional area of one aromatic core (ca. 22 \AA^2). Hence, the efficient packing of the aromatic core in the smectic layer is the dominating ordering force despite the laterally protruding oxyethylene chains which could be intertwined within the layer just as in the crystalline phase of **1a** to maximise the filling of space.

There are different possibilities to consider for the layer stacking of **3a**. Although the arrangements shown in Figure 3a and b agree with the observed periodicity, a local packing with the mesogens pointing upwards and downwards (Fig. 3a) is not consistent with the existence of the SmC phase and there is no signal

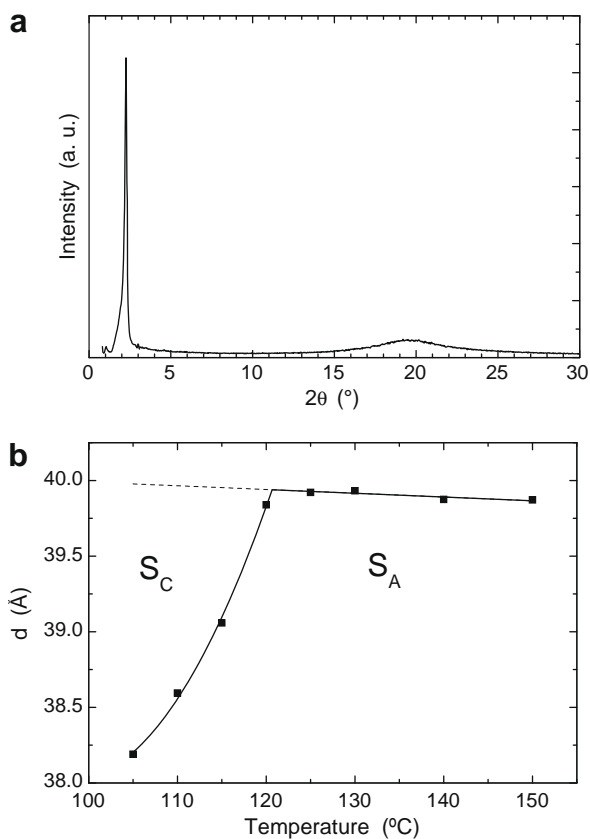


Figure 2. (a) X-ray pattern of **3a** in the SmA phase at 130°C . (b) X-ray temperature dependence on heating of the lamellar distance of **3a**.

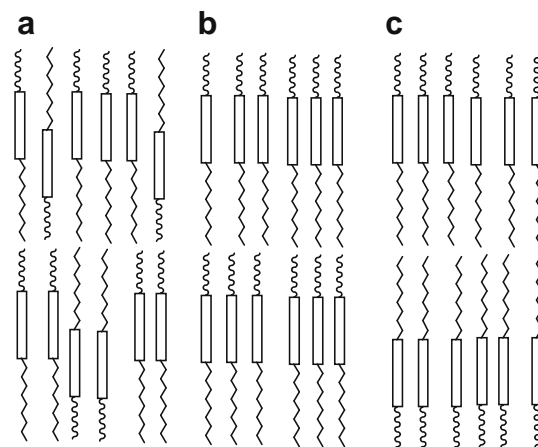


Figure 3. Schematic representations of the SmA phase of **3a**.

in the X-ray pattern which could be associated to any related in-plane periodicity. Moreover, this organisation is not likely to occur due to the expected micro-segregation between aliphatic and oxyethylene chains which are known to exhibit different amphiphatic properties. This later argument can also be used to rule out a single-layer organisation formed by mesogens pointing all upwards (Fig. 3b). The arrangement shown in Figure 3c has the polar and non-polar tails segregated into dipolar interactions that results in a smectic layer periodicity near 80 \AA . However, only a sharp reflection corresponding to $d = 39.1\text{ \AA}$ was again observed in low angle part of the diffraction patterns obtained with a Guinier camera that could record periodicities up to 90 \AA . Likely, the organisation is locally of the double layer type, but with a correlation distance ($d/2 = L$) associated to the distinction of the aliphatic and oxyethylene sublayers shorter than the overall correlation length d associated to the smectic organisation. This would explain the absence of the reflection associated to the double layer and be satisfactory upon the expected micro-segregation of aliphatic and oxyethylene tails.

The comparison between the mesomorphic behaviours of the calamitic **3a** and dimer **5a** with those of their fully aliphatic analogues **3b** and **5b** can be done to assess the effect of the oxyethylene terminal tail on the smectic phase stabilities. Indeed, the data given in Table 1 show that the global mesomorphic behaviour of the two pairs of compounds does not depend on the terminal chain nature but rather on the overall molecular architecture. Thus, both **3a** and **3b** show SmC and SmA phases with comparable transition enthalpies, while both **5a** and **5b** show non-tilted smectic phases (SmB with mosaic textures containing homeotropic domains/SmA with focal conic and homeotropic textures) and nematic phase with comparable transition enthalpies. Despite the fact that the smectic phase stability is somewhat reduced, **3a** still shows an appreciable smectic range. But the presence of two oxyethylene tails in the dimer **5a** significantly decreases the smectic range, most probably due to its symmetric molecular design (polar/rigid/non-polar/rigid/polar).

Therefore, although we are aware that the real conformations could be changed by the neighbourhood molecules, and therefore the application of calculated conformations should be handled with care, the combination of experimental and modelling information on these three-block polyphilic molecules indicates that a substantial fraction of *gauche* conformations persist in the oxyethylene chains up to the isotropisation temperatures; and that their presence does not prevent the occurrence of lamellar organisations provided that amphiphaticity is preserved in the molecular design. In this context, **1a** is a valuable smectogenic building block for amphiphatic functional organic materials.

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Supplementary data

Experimental and computational details, full synthetic procedures and ^1H NMR and ^{13}C NMR characterisation are given in the Supplementary data. DSC and selected X-ray patterns and textures of **1a** and **3a** are also included. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2009.07.002](https://doi.org/10.1016/j.tetlet.2009.07.002).

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11. The molecular volume was calculated with the assumption of additivity of the partial volume of the constituent parts of **3a**. (see Ref. 10). The crystallographic data provide a $V = 425 \text{ \AA}^3$ for **1a** which is the oxyethylene-biphenyl moiety of **3a**. The phenoxy volume plus the 12-carbon tail volume amounts to 489 \AA^3 . After the correction for expansion of the methylenes with temperature, the volume of **3a** at $120 \text{ }^\circ\text{C}$ is 953 \AA^3 .