On the supramolecular packing of bent-shaped molecules: the influence of the central bent-core on the liquid crystalline behaviour†

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Two series of bent-shaped molecules have been synthesized and their supramolecular self-organization at variable temperature has been studied. The majority of these bent-compounds form liquid crystalline phases and the mesomorphic behaviour of them has been fully characterized by polarised optical microscopy, calorimetry, X-ray diffraction and dielectric techniques. A series of bis-4-*n*-tetradecyloxybenzoyloxybenzoates derived from naphthalene, resulting in a change of the bending angle, have proved that when these cores bend around 120°, a polar lamellar packing (SmC$_a$P$_A$) can be induced, whereas when the angle was around 60°, an orthogonal lamellar arrangement (SmA) that responded to an electric field, are found to occur. Liquid-crystal order can also be achieved over a significant range of temperatures by using appropriate bis-4,4′-disubstituted phenylene derivatives (–Ar–X–Ar–). Groups such as –CO–, SO– and –CH$_2$– connecting the aromatic rings induce the SmC$_a$P$_A$ phase while a sulfide group (–S–) leads to columnar order. Further, the formation of isotropic textures as chiral conglomerates or a field-induced phase transition have also been observed as unusual properties of the self-organizations of these compounds.

Introduction

Since 1996, when Niori *et al.*[1] reported for the first time on self-organization of achiral bent-core molecules resulting in new liquid crystalline phases (also known as banana-shaped liquid crystals), a rising interest has grown on them, due essentially to the unusual properties of these new materials regarding both polarity and chirality.

Because of the particular shape of these molecules, a restricted rotation around the molecular long axis is generated that gives rise to a macroscopic polarization in the smectic layers or columns. Furthermore, in the tilted phases formed by these bent-core molecules the combination of polar order and director tilt leads to a chiral structure of the layers without the presence of chiral molecules.[2]

The singularities of these self-organizing supramolecular systems have attracted the attention from academics, and several highlights and review papers have been published in the last few years.[3] Additionally their potential has also been pointed out for applications in fields such as electrooptics and nonlinear optics materials, where organic compounds have provided exceptional contributions by appropriate molecular design.[4]

In order to control the supramolecular packing of bent-shaped molecules an extensive range of structural modifications have been made on the general structure of this type of compounds, regarding the terminal chains, the lateral moieties and the central bent core (see Fig. 1 and 2).

The lateral cores have been widely modified. Both the nature and sense of the links between the lateral aromatic rings have been probed to be useful tools to control the molecular arrangements.[3*a*,*e*,5] Furthermore, the variation of the number of lateral aromatic rings and the incorporation of substituents in them (specially halides) have also become a very attractive target for researchers.[6] Concerning terminal chains, apart from several structure–mesomorphic properties relationship studies where the length of the terminal chains is modified (namely alkyl or alkoxy chains with 2 up to 22 carbons),[7] examples of terminal chains incorporating chiral centers,[8] bulky silicon-containing groups,[9] polymerizable moieties[10] as well as some polycatenar systems[11] have been reported.

Finally, regarding the central core the modifications are mainly related with the rigidity and the polarity of this moiety. Typical mesomorphism of bent-shaped compounds has been

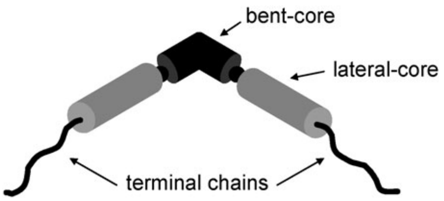

Fig. 1 General structure of bent-shaped molecule that form bent-core liquid crystals.

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† Electronic supplementary information (ESI) available: 1: Graphical comparison of imine *vs.* ester naphthalene series. 2: Conformations and theoretical molecular lengths of **N(2,3)** and **N(2,7)**. 3: Switching curves of **N(2,7)**. 4: DSC curves, X-ray diffractograms and microphotographs of selected compounds. See DOI: 10.1039/b9nj00230h

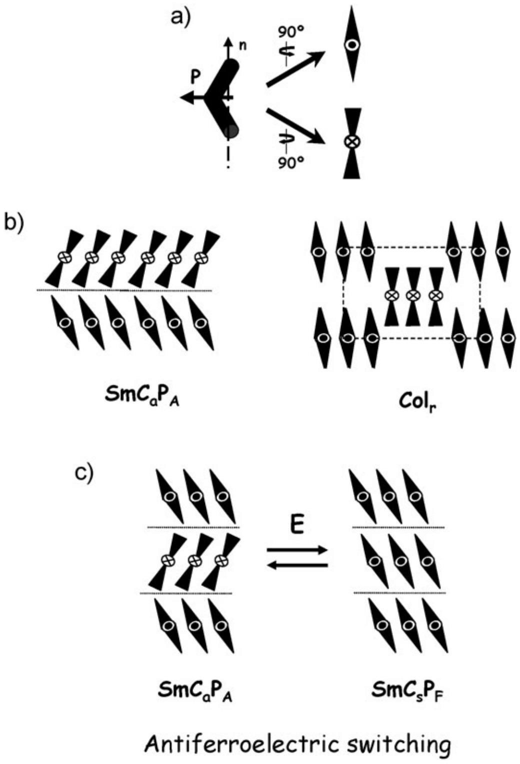


Fig. 2 Schematic representations used for bent-shaped molecules (a). Models proposed for some of the arrangements, in the SmCP and Col$_r$ packings (b). Schematic representations of the antiferroelectric switching of a SmC$_a$P$_A$ and SmC$_s$P$_F$ mesophase induced by applying an electric field (c).

observed in molecules where the central core consists of 1,3-disubstituted benzene, 2,6-disubstituted pyridine, 2,7-disubstituted naphthalene or 3,4′-disubstituted biphenyl rings.[3] In these cases, a bent-core angle of about 120° is generated, which is considered the optimal angle to promote compact packing affording polar mesophases. Nevertheless the bending angle can be varied in the range between 105 and 140° leading to mesomorphism. Thus the presence of a substituted six-membered central aromatic ring (with halogens, methyl or nitro groups)[3,12] or alternatively the presence of five-membered ring heterocycles[13] cause a distortion of the bent angle. On the other hand, recent interest has also been focused on the search of "banana"-like mesomorphism for molecules showing a very acute central angle such as for 1,7-dihydroxynaphthalene derivatives.[8f,14]

Beside this, more flexible structures, either cyclic[15] or odd acyclic[16] aliphatic spacers as well as single point examples of linking units such as –CH$_2$–, –CO–, –S–, –O– or –CH$_2$OOC– have been used by some authors to promote this type of supramolecular packing.[17]

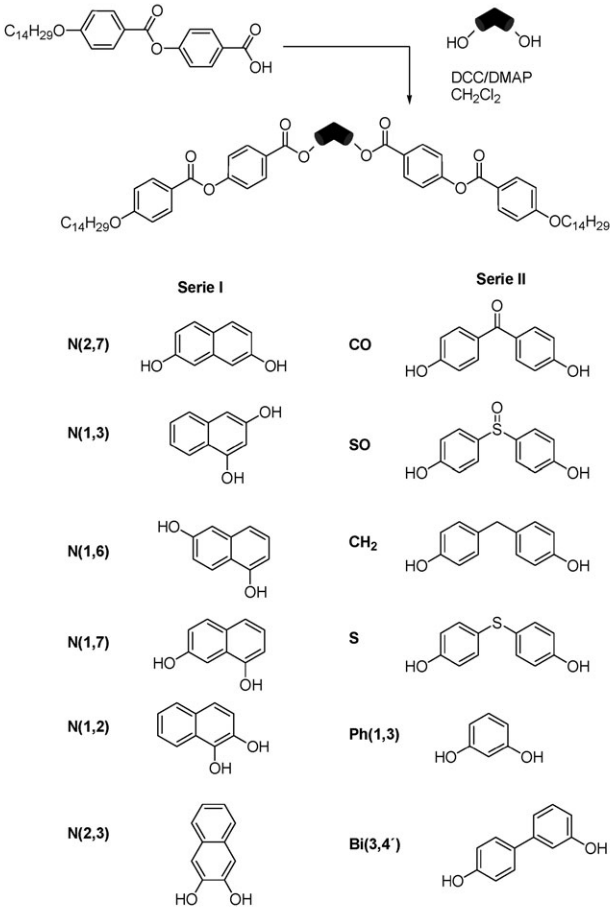
With the aim of going deeper in the supramolecular packing of some of these scarcely studied bent-core structures herein, we describe and discuss the ability of different bent-shaped molecules to show liquid crystal behaviour.

The compounds selected for this study have been divided in two series (Scheme 1). Series I contains a group of central naphthalene derivatives where the aromatic system has been substituted in different positions, namely 2,7- **N(2,7)**, 1,3- **N(1,3)**, 1,6- **N(1,6)**, 1,7- **N(1,7)**, 1,2- **N(1,2)** and 2,3- **N(2,3)** while series II, contains different *p*-disubstituted phenylene rings linked by methylene (**CH$_2$**), carbonyl (**CO**), sulfide (**S**) and sulfoxide (**SO**) groups as central moieties.

All compounds bear 4-*n*-tetradecyloxybenzoyloxybenzoates as lateral structures, selected because of its well-known tendency to induce wide bent-core mesophase ranges, low transition temperatures as well as a high chemical stability.[3]

The interest on these structures arises because they may open new possibilities for the design of mesogenic bent-core structures. Moreover, the results can be also extended to other self-organizing supramolecular systems, such as SAM or LB films.[18] On one hand, few naphthalene derivatives different from 2,7-substitutions have been studied so far,[8f,14,19] even though they will allow different bending angles by changing substitution on the aromatic structure. On the other hand, they can be considered suitable candidates to introduce substituents on the central aromatic core in an easy way without varying significantly the length (*L*)/diameter (*d*) ratio, in contrast with what happens with 1,3-phenylene derivatives.

Concerning bis-4,4′-disubstituted phenylenes, future possibilities could be proposed for them, not only on changing the typical 120° angle by using –S– and –CH$_2$– moieties but also by introducing either strong polarity and chirality in the apex position by modifying the carbonyl or sulfoxide center.



Scheme 1 The synthetic route and the schematic representation of the two series of bent-shaped compounds studied.

Synthesis

All the final compounds were prepared by condensation of the 4-(4-*n*-tetradecyloxybenzoyloxy)benzoic acid with the corresponding diphenol using the DCC/DMAP method as shown in Scheme 1. All the diphenols were purchased from Sigma-Aldrich, except for 3,4′-dihydroxybiphenyl that was prepared as described before[20] and 4,4′-bisphenol sulfoxide that was obtained by oxidation of the 4,4′ thiobisphenol using the method described by Engman.[21] Mesomorphic, electrooptic and optical properties of compounds **CH$_2$** and **S** have already been described. However, their synthesis and structural characterization is described here for the first time.

Results and discussion

Liquid crystalline properties

All of the new compounds reported here were studied by polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) at variable temperature in order to characterize their liquid crystalline behaviour. Furthermore, the electro-optic responses of the different materials were also investigated by POM under an electric field in order to obtain additional information about the liquid crystalline phases formed by these molecules and their ability to switch under electric fields. The results obtained using the different techniques led us to assign the liquid crystalline properties gathered in Table 1 for these compounds. For the sake of comparative analysis, the properties of the related materials **Bi(3,4′)**[20] and **Ph(1,3)**[20] are also included in this table.

As it can be seen, all the materials studied here exhibit liquid crystalline mesophases characteristic of bent-cores except for compounds **N(1,3)** and **N(1,7)**. Enthalpy values for the mesophase–isotropic liquid transitions are in the range 17–28 kJ mol^{-1}, according to values reported for this type of phase transition. Mesomorphic behaviour will be analysed within the same series of compounds.

Table 1 Transition temperatures (T/°C) and enthalpies (ΔH/kJ mol^{-1}) for compounds **N(2,7)**, **N(1,3)**, **N(1,6)**, **N(1,7)**, **N(1,2)**, **N(2,3)**, **CO**, **SO**, **CH$_2$**, **S**, **Ph(1,3)** and **Bi(3,4′)**

Compound	Phase transition/°C (ΔH/kJ mol^{-1})^{ab}
N(2,7)	C • 103.0 (51.9) • SmC$_a$P$_A$ • 118.0 (25.2) • I I • 115.7 (26.3) • SmC$_a$P$_A$ • 87.8 (52.3) • C
N(1,3)	C • 127.9 (73.8) • I I • 105.1 (40.5) • C
N(1,6)	C • 110.1 (27.4) • SmC$_a$P$_A$ • 148.2 (26.4) • I I • 145.2 (26.9) • SmC$_a$P$_A$ • 95.3 (24.4) • C
N(1,7)	C • 145.0 (15.4) • C′ • 155.2 (54.0) • I I • 149.0 (54.2) • C′ • 132.0 (13.7) • C
N(1,2)	C • 87.8 (29.8) • SmA • 158.2 (12.2) • I I • 153.2 (12.6) • SmA • 34.1 (7.5) • C
N(2,3)	C • 127.3 (54.6) • SmA • 210.6 • N • 211.6 (7.4)^c • I I • 211.3 • N • 210.5 (7.8)^c • SmA • 75.0 (44.8) • C
CO	C • 155.6 (21.4) • SmC$_a$P$_A$ • 195.3 (19.0) • I I • 195.3 (17.7) • SmC$_a$P$_A$ • 141.5 (22.8) • C
SO	C • 143.5 (34.6) • SmC$_a$P$_A$ • 162.2 (25.9) • I I • 161.1 (25.6) • SmC$_a$P$_A$ • 124.2 (36.0) • C
CH$_2$	C • 123.9 (60.5) • SmC$_a$P$_A$ • 161.6 (28.0) • I I • 160.5 (27.6) • SmC$_a$P$_A$ • 108.5 (30.2) • C
S	C • 150.8 • Col$_r$ • 156.2 (45.8)^d • I I • 154.9 (25.3) • Col$_r$ • 148.1 (22.9) • C
Ph(1,3)[20]	C • 103.9 (50.9) • SmC$_a$P$_A$ • 118.3 (25.5) • I I • 116.5 (24.9) • SmC$_a$P$_A$ • 88.8 (49.6) • C
Bi(3,4′)[20]	C • 74.2 (21.4) • SmC$_a$P$_A$ • 156.9 (27.9) • I I • 156.5 (27.1) • SmC$_a$P$_A$ • 67.7 (17.5) • C

[a] Data determined by DSC, from second scans at a scanning rate of 10 °C min^{-1}. [b] Cr: crystal, SmA: smectic A mesophase, N: nematic mesophase, Col$_r$: columnar rectangular mesophase, SmC$_a$P$_A$: smectic C anticlinic polar antiferroelectric mesophase, I: isotropic liquid. [c] Combined enthalpy for SmA–N–I transition. [d] Combined enthalpy for C–Col$_r$–I transition.

(a) Series I: naphthalene derivatives. The mesomorphic behaviour of compounds of this series is highly influenced by the position of the lateral cores around the naphthalene system, that is, by the bending angle generated between them. For compounds **N(2,7)**, **N(1,3)** and **N(1,6)**, a molecular bending angle of approximately 120° is afforded. Compounds **N(2,7)** and **N(1,6)**, exhibit typical texture of the polar smectic C mesophase, growing from the isotropic liquid as concentric defects to develop a grainy texture. However, compound **N(1,3)** shows no mesomorphic behaviour even though the angle is similar to that of the other two compounds. This could be attributed to the fact that the two lateral cores are connected to the same aromatic core in such a way that the second aromatic ring acts as a bulky group disturbing the compact packing of the molecules leading to the bent-core liquid crystal phase. The smectic mesophase of compounds **N(2,7)** and **N(1,6)** was assigned as the antiferroelectric anticlinal variety (SmC$_a$P$_A$) (Fig. 2 and 3(a)) by the characteristic textures observed by optical microscopy and complementary dielectric studies revealing their antiferroelectric switching (see ESI†). XRD studies confirm the smectic nature of the mesophase and allowed us to calculate a layer spacing of 39 Å for both compounds. By evaluating the theorical length of the molecules by stereomodels (considering all-*trans* conformation of the terminal chains, see ESI†) it was possible to calculate a tilt angle of 50° (Table 2) typical for molecules in the SmCP phase.

When comparing the range of mesophase of compounds **N(2,7)** and **N(1,6)** with that of parent compounds **Bi(3,4′)** and **Ph(1,3)** (included in this study for comparative reasons) it is possible to conclude that compounds **N(2,7)** and **Ph(1,3)** provide a similar mesogenic range, whereas **N(1,6)** and **Bi(3,4′)** show the widest but similar range. It is worth mentioning that when increasing the asymmetry of the molecule (as for compounds **N(1,6)** and **Bi(3,4′)**), a stabilization of the mesophase is achieved as well as a remarkable increase in the range of mesophase. Furthermore, 1,6-naphthalene could be considered as an attractive alternative to the broadly used 3,4′-biphenylene structure.

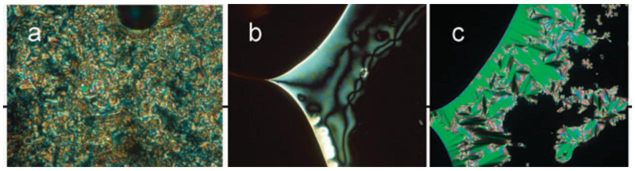


Fig. 3 Photomicrographs of the textures of the (a) SmCP phase of **N(1,6)** at 146 °C and of the nematic (b) and SmA (c) phases of **N(2,3)** at 210 and 207 °C, respectively, between glass plates.

Table 2 X-Ray diffraction data for the mesophases of the compounds **N(2,7)**, **N(1,6)**, **N(1,2)**, **N(2,3)**, **CO**, **SO**, **CH_2** and **S**

Compound	Phase	Parameters Å (exptl.)	L^a/Å (theor.)	Layer spacing/Å	Miller indices
N(2,7)	SmCP	*c*: 39.6	69.8	39.2	001
				20.1	002
				13.1	003
N(1,6)	SmCP	*c*: 39.0	68.6	39.0	001
N(1,2)	SmA	*c*: 33.9	56.8 (38.5)^b	33.9	001
N(2,3)	SmA	*c*: 33.3	56.6 (37.5)^b	33.3	001
CO	SmCP	*c*: 42.8	72.5	42.8	001
				21.4	002
SO	SmCP	*c*: 49.4	73.0	49.4	001
				24.7	002
				16.5	003
CH_2	SmCP	*c*: 46.2	72.5	46.2	001
				23.1	002
				15.4	003
S	Col_r	*a*: 83	72.9	43.8	101
		c: 51.5		25.8	002
				20.8	400
				16.1	103

[a] Molecular length calculated considering extended conformation of terminal chains. [b] In parentheses, length corresponding to half molecule.

When the angle is reduced to approximately 60°, as for compounds **N(1,7)**, **N(1,2)** and **N(2,3)** (substitutions 1,7-, 1,2- and 2,3- on the naphthalene unit, respectively), mesomorphic behaviour is observed for two out of the three compounds.

Compound **N(1,7)** showed only one peak in the DSC thermogram on the heating process corresponding to a crystal to isotropic liquid transition. However, textures consistent with a smectic A mesophase (SmA) were observed under POM for the compounds **N(1,2)** and **N(2,3)** as fan-shaped textures were formed (Fig. 3(c)). In both cases, the mesophase was stable over a very wide range of temperatures. It is remarkable that even if the bent angle is similar for both compounds, the breaking of the symmetry in the case of compound **N(1,2)** decreased significantly the transition temperatures for this material. On the other hand, compound **N(2,3)** exhibits also a very short range of enantiotropic nematic mesophase above the SmA as could be detected by the appearance of typical nematic droplets on slow cooling from the isotropic liquid. This mesophase was confirmed by a small peak on the DSC thermogram. However, it was not possible to obtain an X-ray diffractogram of this phase due to the very short range of temperature in which it appears. X-Ray diffractograms of the SmA mesophase showed only one strong reflection in the short range angle region corresponding to a layer spacing of 34 and 33 Å for compounds **N(1,2)** and **N(2,3)**, respectively. These values are close to that calculated theoretically for a half molecule so pointing to an arrangement like that shown in Fig. 4(c).

Furthermore, the behaviour of the mesophase of the compounds **N(1,2)** and **N(2,3)** under an electric field was studied in 5 μm Linkam commercial cells. For compound **N(2,3)**, initially on cooling from the isotropic phase, the sample showed a birefringent semi-aligned texture with few defects (Fig. 5(a)). When applying an increasing electric field to the sample, yellow stripes appeared perpendicular to the alignment direction of the sample (Fig. 5(b)). When a higher voltage was reached (150 V_{pp}), the stripes almost disappeared and the texture became black (Fig. 5(c)).

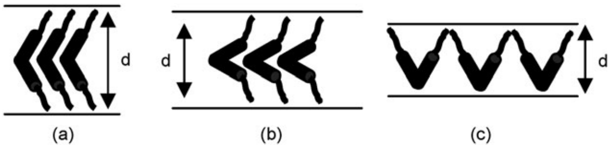


Fig. 4 Different schematic drawings of the molecules proposed for the SmA mesophase induced by bent-core molecules: for a SmAP mesophase (a) and for a calamitic SmA mesophase (b, c) (any polar arrangement is proposed in this case).

Similar behaviour was observed for compound **N(1,2)**. In this case, initially on cooling the isotropic liquid a poorly aligned texture showing several defects was obtained and a higher electric field (up to 240 V_{pp}) is necessary to reach the black texture (Fig. 5(f)–(j)). In both cases, when removing the electric field, no changes are observed, even when uncrossing the polarizers. These behaviours indicate that there might be a reorientation of the molecules induced by the electric field. However there is not any experimental data to confirm the

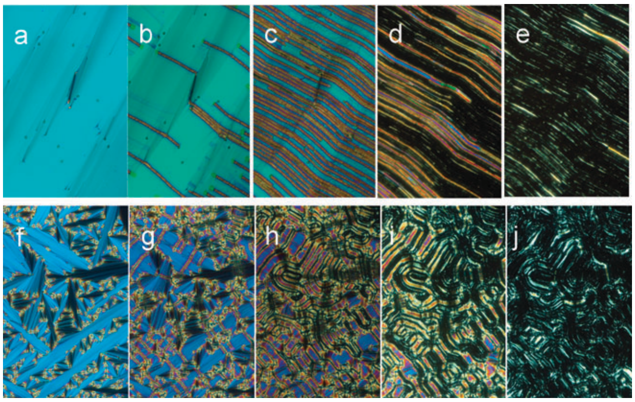


Fig. 5 Microphotographs in 5 μm commercial Linkam cell of compounds: (top) **N(2,3)** at 207 °C applying no electric field (a) and applying (b) 120 V_{pp}, (c) 130 V_{pp}, (d) 140 V_{pp} and (e) 150 V_{pp} of AC voltage at 1 Hz; (bottom) **N(1,2)** at 164 °C applying no electric field (i) and applying (j) 200 V_{pp}, (k) 220 V_{pp}, (l) 230 V_{pp} and (e) 240 V_{pp}.

presence of a SmAP phase. No current peak was detected when applying electric field. Further studies in order to analyze the dielectric and electro-optic behaviour for these compounds are being carried out.

As the molecular angle is small and the central core bulky, the molecules can not be packed one inside the other as is usually proposed for bent-core mesophases and a classical parallel orthogonal packing is likely present (Fig. 4(a)). Under such conditions a smectic A arrangement could be achieved if molecules are assembled, for example, in one of the dispositions shown in Fig. 4(b) or (c).

When comparing the mesogenic behaviour of this series of compounds with those observed for imine-based analogues reported by Lee *et al.*,[14b] significant differences are observed (see ESI†). In the case of 2,7- and 1,6-substitutions a remarkable decrease in the clearing points, with a significant reduction of mesophase range, is achieved when changing from imine to ester. However, only a slight decrease on the clearing points is noticed for the other compounds of the series. Concerning the mesophases, it is worth mentioning the appearance of the B4 phase for some of the imine derivatives, which could not be detected for the ester analogues. Further, **N(2,3)** showed a nematic phase, not described for the imine homologue. Liquid crystalline phases were not formed for the (1,7) or (1,3) derivatives in either of the series.

(b) Series II: bis-4,4′-disubstituted phenylene derivatives. In the case of compounds of series II, all of them exhibit liquid crystalline properties, irrespective of their angular structure. Compounds **CO** and **SO** showed a SmC_aP_A mesophase as could be assigned by electrooptical and dielectric measurements. Although both compounds have rather similar structures and show a similar mesomorphic behaviour, compound **CO**, bearing the carbonyl moiety, leads to a slight stabilization of both the solid and the liquid crystal phases.

Likewise, the X-ray patterns of these two compounds in the mesophase showed up to three reflections at periodic distances in the small-angle region in addition to a diffuse wide angle scattering (see Table 2). Layer spacings of 43 and 49 Å were measured experimentally at the SmCP phase for compounds **CO** and **SO**, respectively. When comparing experimental values with those determined theoretically using stereomodels (considering extended conformation of the terminal chains), it was possible to calculate tilting angles of around 49 and 41°, respectively.

Compounds $\mathbf{CH_2}$ and **S** can be related to **CO** and **SO**. In the later cases, hybridization of the central atom was changed from sp^2 to sp^3 (for $\mathbf{CH_2}$ and **S**) which involves variations in both angle and conformational freedom, as well as, previously mentioned, their polar and chiral potentials. Compounds $\mathbf{CH_2}$ and **S** form bent-core mesophases. Even though the methylene-derivated core ($\mathbf{CH_2}$) is more flexible than the carbonyl one and much more than the other aromatic cores studied in this paper, compound $\mathbf{CH_2}$ still shows a wide range of SmCP mesophase. The antiferroelectric anticlinal nature of this mesophase was confirmed by electrooptical and dielectric measurements. X-Ray diffraction patterns show up to three reflections in the small-angle region in addition to a diffuse wide angle scattering. A layer spacing of 46 Å and a tilting angle of 45° could be calculated for this compound. The mesophase of this compound was studied in detail and results are gathered elsewhere.[22]

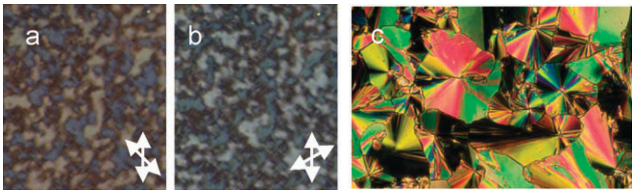


Fig. 6 Photomicrographs of the texture of (a) SmCP phase of compound **CO** at 180 °C when uncrossing polarizers (a) left and (b) right. (c) columnar mesophase of compound **S** at 152 °C.

A columnar phase was detected for compound **S** in a very short range of mesophase. A mosaic texture was observed under POM (see Fig. 6(c)) when cooling from the isotropic liquid and up to four reflections in the X-ray diffraction pattern were detected, which could be indexed to a rectangular columnar cell which lattice parameters a = 83 Å and c = 51.5 Å.

When applying an electric field to the columnar mesophase of this compound, a clear electro-optical switching was observed. This behaviour has been studied in detail concluding that a transition from a columnar to a SmCP mesophase has taken place induced by the electric field as has been published elsewhere.[22b]

Interestingly, both carbonyl (–CO–) and methylene ($-CH_2-$) central bent-cores generate an isotropic texture for the SmCP mesophase, with dark conglomerates where domains of different chirality are observed when uncrossing the polarizers (see Fig. 6(a) and (b)). However, the transition temperatures are significantly lower for the methylene derivative as could be expected from the stronger polar nature of the CO group. In the case of the sulfur derivatives (**SO** and **S**), the behaviour is slightly different when substituting sulfoxide for the less rigid sulfur atom. A columnar mesophase in very narrow interval of temperature is obtained instead of the SmCP mesophase assigned for compound **SO**, however, a very similar range of mesophases are induced by the two compounds. This fact indicates a remarkable effect of the central moiety on the packing of the molecules hindering a lamellar arrangement for compound **S**, only reached under application of an electric field.

Conclusions

Two different series of bent-shaped molecules have been prepared and their supramolecular self-organization at variable temperature has been studied.

In order to readily control the bent-shaped molecular packing, naphthalene has been used as the origin of bent-central cores. Different bis-4-*n*-tetradecyloxybenzoyloxybenzoates resulting in a change of the bending angle proved that when the bending angle was around 120°, SmCP mesomorphism can be induced, whereas when the angle was much smaller, around 60°, a SmA phase that shows a response under electric field occurred. However, it seems that not only the angle is determining in the mesomorphic behaviour as some of the compounds are crystalline even if they show similar bending angle. The wide ranges of mesophase determined, together with the number of available positions for substituents, open interesting possibilities for naphthalene central cores to be used as bending units to generate polar order and mesomorphism.

On the other hand, bent-core mesomorphism can be also achieved over a significant range of temperatures by using appropriate bis-4,4′-disubstituted phenylene derivatives. Groups such as –CO–, –SO– and –CH$_2$– connecting them induce the SmCP phase and a sulfide group (–S–) leads to columnar order. Besides, two compounds (**CO** and **CH$_2$**) show isotropic texture with dark conglomerates, while one of them (**S**) exhibits a Col$_r$–SmCP change upon applying a high enough electric field.

Experimental

Infrared spectra for all the compounds were obtained using ATI Mattson (FTIR) and Nicolet Avatar 360 (FTIR) spectrophotometers in the 400–4000 cm^{-1} spectral range. ^{1}H and ^{13}C NMR spectra were recorded on Bruker ARX-300 MHz, Bruker AV-400 MHz and AV-500 MHz spectrometers and samples were in solution. Elemental analyses were performed on a Perkin-Elmer 240 analyzer. Mass spectrometry studies (FAB+, MALDI+) were performed with a VG AutoSpec EBE and a Microflex (MALDI-ToF). Commercial chemicals (reagent grade) were purchased from Aldrich Chemical Co., Fluka or Panreac and used without further purification. Solvents were purified and dried by standard techniques.

Mesomorphic properties were studied by optical microscopy using an Olympus BH2 microscope with crossed polarizers. The microscope was connected to a Linkam THMS 600 hot stage and an Olympus DP-12 camera. Transition temperatures were determined by differential scanning calorimetry (DSC) using TA2910, DSC Q20, DSC Q1000 or DSC Q2000 differential calorimeters calibrated with indium (156.6 °C, 28.44 J g^{-1}). X-Ray diffraction patterns were obtained with an evacuated Pinhole Camera (Anton–Paar) operating with a point-focused Ni-filtered Cu-Kα beam. The samples were held in Lindemann glass capillaries (1 mm diameter) and heated, where necessary, with a variable-temperature attachment. The diffraction patterns were collected on flat photographic film. Polarization measurements were carried out using commercial cells with ITO electrodes coated with polyimide (LINKAM, 5 μm). The triangular wave voltage was supplied by an HP3245A function generator plus an amplifier and the current was recorded using an IO tech 488/6A multimeter. All the equipment was controlled with a Fujitsu S-325 generator and a Tektronix TDS 310 oscilloscope.

General synthetic procedure used to prepare bent-shaped compounds

DCC (1.1 mmol) was added to a cooled (0 °C), stirred mixture of the corresponding diphenol (0.39 mmol), 4-(4-tetradecyloxybenzoyloxy)benzoic acid (1 mmol) and DMAP (0.5 mmol) in dichloromethane (20 mL) under an argon atmosphere. The reaction mixture was stirred for 30 min at 0 °C and then allowed to warm to room temperature. The mixture was stirred for 24 h, the resulting solid was filtered off and the filtrate was evaporated to give a solid, which was purified by flash chromatography on silica gel, using dichloromethane as the eluent. The solid was crystallized twice, first from toluene and then from ethyl acetate.

2,7-Bis[4-(4-*n*-tetradecyloxybenzoyloxy)benzoyloxy]naphthalene N(2,7)). Yield: 25%. R_f (hexanes–ethyl acetate 8 : 2): 0.5. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.86 (t, J = 6.5 Hz, 6H); 1.20–1.38 (m, 44H); 1.77–1.84 (m, 4H); 4.03 (t, J = 6.7 Hz, 4H); 6.96 (d, J = 8.7 Hz, 4H), 7.15–7.18 (m, 4H); 7.35 (d, J = 9.0 Hz, 4H); 7.48 (d, J = 7.8 Hz, 2H); 8.12 (d, J = 8.7 Hz, 4H); 8.26 (d, J = 9.0 Hz, 4H). ^{13}C NMR (300 MHz, CDCl$_3$) δ 14.2, 22.7, 26.1, 29.4, 29.4, 29.5, 29.6, 29.7, 31.9, 68.5, 100.0, 114.4, 115.9, 119.4, 121.0, 122.2, 126.7, 129.9, 131.9, 132.4, 151.5, 155.6,163.8, 164.2, 164.4. IR (Nujol, NaCl): 1734, 1722, 1678, 1600, 1463, 1161, 1055 cm^{-1}. EA for $C_{66}H_{80}O_{10}$: calc.: C 76.74%, H 7.75%; found: C 76.84, H 7.99%. MS (FAB+) *m*/*z*: 317, 367, 437.

1,3-Bis[4-(4-*n*-tetradecyloxybenzoyloxy)benzoyloxy]naphthalene (N(1,3)). Yield: 64%. R_f (dichloromethane–hexanes 9 : 1): 0.17. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.88 (t, J = 6.8 Hz, 6H); 1.27–1.57 (m, 44H); 1.81–1.85 (m, 4H); 4.05 (t, J = 6.4 Hz, 4H); 7.00 (dd, J = 2.8 Hz, J = 8.8 Hz, 4H), 7.38–7.44 (m, 5H); 7.50–7.58 (m, 2H); 7.70–7.72 (m, 1H); 7.90 (d, J = 8.0 Hz, 1H); 7.97 (d, J = 8.0 Hz, 1H); 8.15–8.19 (m, 4H); 8.32 (d, J = 8.4 Hz, 2H); 8.41 (d, J = 8.4 Hz, 2H). ^{13}C NMR (400 MHz, CDCl$_3$) δ 14.1, 22.7, 26.0, 29.1, 29.4, 29.6, 29.6, 29.7, 29.7, 29.7, 31.9, 68.4, 114.3, 114.4, 116.9, 121.0 121.0, 121.5, 122.1, 122.3, 125.3, 126.4, 126.5, 126.7, 127.4, 128.0, 131.9, 132.0, 132.4, 132.5, 134.4, 147.5, 147.9, 155.6, 155.7, 163.8, 163.9, 164.0, 164.2, 164.3. IR (Nujol, NaCl): 2920, 2851, 1736, 1604, 1467, 1258, 1207, 1162, 1067 cm^{-1}. EA for $C_{66}H_{80}O_{10}$: calc.: C 76.71%, H 7.80%; found: C 76.81%, H 7.81%. MS (FAB+) *m*/*z*: 368, 451, 1056.

1,6-Bis[4-(4-*n*-tetradecyloxybenzoyloxy)benzoyloxy]naphthalene (N(1,6)). Yield: 50%. R_f (dichloromethane–hexanes 9 : 1): 0.54. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.88 (t, J = 6.8 Hz, 6H); 1.27–1.55 (m, 44H); 1.79–1.87 (m, 4H); 4.06 (t, J = 6.8 Hz, 4H); 6.98–7.01 (m, 4H), 7.38–7.44 (m, 6H); 7.58 (dd, J = 7.6 Hz, J = 8.4 Hz, 1H); 7.78–7.81 (m, 2H); 8.02 (d, J = 9.2 Hz, 1H); 8.15–8.19 (m, 4H); 8.32–8.34 (m, 2H); 8.41–8.43 (m, 2H). ^{13}C NMR (300 MHz, CDCl$_3$) δ 14.1, 22.7, 26.0, 29.1, 29.3, 29.6, 29.6, 29.7, 29.7, 29.7, 31.9, 68.4, 114.4, 121.0 121.0, 122.1, 122.3, 125.4, 126.0, 126.6, 127.6, 131.9, 132.0, 132.4, 132.5, 132.8, 146.6, 149.3, 155.5, 155.6, 163.8, 163.8, 164.4. IR (Nujol, NaCl): 2920, 2850, 1736, 1603, 1255, 1202, 1162, 1061 cm^{-1}. EA for $C_{66}H_{80}O_{10}$: calc.: C 76.71%, H 7.80%; found: C 76.57%, H 7.66%. MS (FAB+) *m*/*z*: 317, 451, 1056.

1,7-Bis[4-(4-*n*-tetradecyloxybenzoyloxy)benzoyloxy]naphthalene (N(1,7)). Yield: 49%. R_f (dichloromethane–hexanes 8 : 2): 0.28. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.88 (t, J = 6.8 Hz, 6H); 1.26–1.50 (m, 44H); 1.79–1.86 (m, 4H); 4.05 (t, J = 6.8 Hz, 4H); 6.97–6.99 (m, 4H), 7.35–7.45 (m, 6H); 7.55 (dd, J = 7.6 Hz, J = 8.4 Hz, 1H); 7.75 (d, J = 1.6 Hz, 1H);

7.83 (d, J = 8.4 Hz, 1H); 7.99 (d, J = 8.8 Hz, 1H); 8.14–8.16 (m, 4H); 8.29–8.31 (m, 2H); 8.39–8.41(m, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.1, 22.7, 26.0, 29.1, 29.3, 29.6, 29.6, 29.7, 29.7, 29.7, 31.9, 68.4, 114.4, 121.0 121.0, 122.1, 122.3, 125.4, 126.0, 126.6, 127.6, 131.9, 132.0, 132.4, 132.5, 132.8, 146.6, 149.3, 155.5, 155.6, 163.8, 163.8, 164.4. IR (Nujol, NaCl): 2920, 2850, 1736, 1603, 1255, 1202, 1162, 1061 cm^{-1}. EA for $C_{66}H_{80}O_{10}$: calc.: C 76.71%, H 7.80%; found: C 76.50%, H 7.87%. MS (FAB+) m/z: 317, 451, 1056.

1,2-Bis[4-(4-*n*-tetradecyloxybenzoyloxy)benzoyloxy]naphthalene (N(1,2)). Yield: 23%. R_f (dichloromethane–hexanes 9 : 1): 0.14. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, J = 6.8 Hz, 6H); 1.27–1.55 (m, 44H); 1.81–1.84 (m, 4H); 4.06 (t, J = 6.8 Hz, 4H); 6.98–7.01 (m, 4H), 7.27 (d, J = 9.2 Hz, 2H); 7.34 (d, J = 8.8 Hz, 2H); 7.53–7.57 (m, 3H); 7.90 (d, J = 8.8 Hz, 1H); 7.93–7.96 (m, 2H); 8.12–8.16 (m, 4H); 8.19 (d, J = 8.8 Hz, 2H); 8.32 (d, J = 8.8 Hz, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.1, 22.7, 26.0, 29.1, 29.4, 29.5, 29.6, 29.7, 29.7, 29.7, 31.9, 68.4, 114.4, 114.4, 121.0 121.1, 121.4, 121.8, 122.1, 122.2, 125.9, 126.2, 126.3, 126.8, 127.1, 128.0, 131.8, 132.0, 132.4, 132.4, 132.5, 137.4, 139.7, 155.5, 155.7, 163.5, 163.7, 163.8, 163.8, 164.1, 164.2. IR (Nujol, NaCl): 2922, 2852, 1729, 1607, 1465, 1263, 1168, 1063 cm^{-1}. EA for $C_{66}H_{80}O_{10}$: calc.: C 76.71%, H 7.80%; found: C 76.29%, H 7.74%. MS (FAB+) m/z: 317, 451, 1056.

2,3-Bis[4-(4-*n*-tetradecyloxybenzoyloxy)benzoyloxy]naphthalene (N(2,3)). Yield: 80%. R_f (dichloromethane–hexanes 9 : 1): 0.25. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 6H); 1.27–1.58 (m, 44H); 1.80–1.84 (m, 4H); 4.03 (t, J = 6.4 Hz, 4H); 6.95 (d, J = 7.2 Hz, 4H), 7.27 (d, J = 6.8 Hz, 4H); 7.88 (dd, J = 3.2 Hz, J = 6.0 Hz, 2H); 7.86–7.89 (m, 4H); 8.09 (d, J = 7.2 Hz, 4H); 8.16 (d, J = 6.4 Hz, 4H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 14.1, 22.7, 26.0, 29.1, 29.3, 29.6, 29.5, 29.6, 29.7, 31.9, 68.4, 114.4, 121.0 121.1, 122.1, 126.0, 126.5, 127.6, 131.7, 131.8, 132.4, 141.3, 155.5, 163.8, 163.9, 164.2. IR (Nujol, NaCl): 2923, 2853, 1732, 1601, 1465, 1253, 1202, 1161, 1059 cm^{-1}. EA for $C_{66}H_{80}O_{10}$: calc.: C 76.71%, H 7.80%; found: C 76.75%, H 7.65%. MS (FAB+) m/z: 368, 451, 541, 1056.

Bis[4-(4-*n*-tetradecyloxybenzoyloxy)benzoyloxyphenyl] ketone (CO). Yield: 40%. R_f (hexanes–ethyl acetate 8/2): 0.66. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, J = 6.3 Hz, 6H); 1.23–1.42 (m, 44H); 1.80–1.86 (m, 4H); 4.03 (t, J = 6.6 Hz, 4H); 6.97 (d, J 8.7 Hz, 4H); 7.20–7.37 (m, 8H); 7.91 (d, J = 8.7 Hz, 4H); 8.14 (d, J = 8.7 Hz, 4H); 8.28 (d, J = 8.7 Hz, 4H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.1, 22.7, 25.9, 29.1, 29.3, 29.5, 29.6, 29.9, 31.9, 68.4, 109.3, 114.4, 120.9, 121.8, 122.2, 126.4, 131.6, 131.7, 131.9, 132.0, 132.4, 135.1, 154.2, 155.7, 163.9, 164.0, 164.3. IR (Nujol, NaCl): 1730, 1645, 1602, 1462, 1253, 1165 cm^{-1}. EA for $C_{69}H_{82}O_{11}$: calc.: C 76.21%, H 7.60%, S 2.94%; found: C 76.40%, H 7.61%, S 2.61%. MS (FAB+) m/z: 317, 437, 649, 1087.

Bis[4-(4-*n*-tetradecyloxybenzoyloxy)benzoyloxyphenyl] sulfoxide (SO). Yield: 40%. R_f (dichloromethane–ethyl acetate 9 : 1): 0.66. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, J = 6.3 Hz, 6H); 1.23–1.42 (m, 44H); 1.80–1.86 (m, 4H); 4.03 (t, J = 6.6 Hz, 4H); 6.97 (d, J 8.7 Hz, 4H); 7.20–7.37 (m, 8H); 7.91 (d, J = 8.7 Hz, 4H); 8.14 (d, J = 8.7 Hz, 4H); 8.28 (d, J = 8.7 Hz, 4H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.1, 22.7, 25.9, 29.1, 29.3, 29.5, 29.6, 29.9, 31.9, 68.4, 109.3, 114.4, 120.9, 121.8, 122.2, 126.4, 131.6, 131.7, 131.9, 132.0, 132.4, 135.1, 154.2, 155.7, 163.9, 164.0, 164.3. IR (Nujol, NaCl): 1730, 1645, 1602, 1462, 1253, 1165 cm^{-1} EA for $C_{68}H_{82}O_{11}S$: calc.: C 76.21%, H 7.60%, S 2.94%; found: C 76.40%, H 7.61%, S 2.61%. MS (FAB+) m/z: 317, 437, 649, 1087.

Bis[4-(4-*n*-tetradecyloxybenzoyloxy)benzoyloxyphenyl]methane (CH_2). Yield: 51%. R_f (hexanes–ethyl acetate 8 : 2): 0.4. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, J = 6.0 Hz, 6H); 1.25–1.47 (m, 44H); 1.78–1.83 (m, 4H); 4.01– 4.06 (m, 6H); 6.97 (d, J = 8.4 Hz, 4H); 7.15 (d, J = 8.8 Hz, 4H); 7.27 (d, J = 8.8 Hz, 4H); 7.35 (d, J = 8.4 Hz, 4H); 8.15 (d, J = 8.4 Hz, 4H); 8.27 (d, J = 8.4 Hz, 4H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 13.7, 22.2, 25.5, 28.6, 29.1, 29.4, 29.5, 29.6, 29.7, 68.4, 114.4, 120.9, 121.6, 121.7, 122.1, 126.9, 130.0, 131.7, 132.4, 138.4, 149.3, 155.3, 163.8, 164.3, 164.6. IR (Nujol, NaCl): 1727, 1605, 1509, 1463, 1286, 1256, 888, 846 cm^{-1}. EA for $C_{69}H_{84}O_{10}$: calc.: C 77.21%, H 7.89%; found: C 77.00%, H 7.72%. MS (FAB+) m/z: 317, 437, 635, 1073.

Bis[4-(4-*n*-tetradecyloxybenzoyloxy)benzoyloxyphenyl]sulfur (S). Yield: 60%. R_f (dichloromethane–ethyl acetate 9 : 1): 0.52. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.6 Hz, 6H); 1.27–1.48 (m, 44H); 1.80–1.86 (m, 4H); 4.05 (t, J = 6.6 Hz, 4H); 6.99 (d, J = 8.1 Hz, 4H); 7.20 (d, J = 8.1 Hz, 4H); 7.37 (d, J = 8.1 Hz, 4H); 7.43 (d, J = 8.1 Hz, 4H); 8.15 (d, J = 8.1 Hz, 4H); 8.27 (d, J = 8.1 Hz, 4H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.1, 22.7, 25.9, 29.1, 29.3, 29.5, 29.6, 29.9 31.9, 68.4, 109.3, 114.4, 120.9, 122.0, 122.1, 122.6, 126.6, 131.8, 132.2, 132.4, 133.0, 150.1, 155.4, 163.8, 164.2. IR (Nujol, NaCl): 1732, 1607, 1584, 1463, 1397, 1395, 889 cm^{-1}. EA for $C_{68}H_{82}O_{10}S$: calc.: C 74.83%, H 7.57%, S 2.94%; found: C 74.71%, H 7.24%, S 2.61%. MS (FAB+) m/z: 317, 437, 653, 1092.

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