Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Achten, Remko , Cuypers, Ruud , Giesbers, Marcel , Koudijs, Arie , Marcelis Corresponding author, Antonius T. M. and Sudhölter, Ernst J. R.(2004) 'Asymmetric banana-shaped liquid crystals with two different terminal alkoxy chains', Liquid Crystals, 31: 8, 1167 — 1174

To link to this Article: DOI: 10.1080/02678290410001724755

URL: http://dx.doi.org/10.1080/02678290410001724755

LIQUID CRYSTALS, VOL. 31, NO. 8, AUGUST 2004, 1167–1174

Asymmetric banana-shaped liquid crystals with two different terminal alkoxy chains

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(*Received 4 March 2004; accepted 19 April 2004*)

Two series of asymmetric banana-shaped compounds have been synthesized and studied. In the 1,3-phenylene bis[4-(4′-alkoxybenzoyloxy)]benzoate series the lack of symmetry was derived solely from the difference in length of the two terminal alkoxy chains. In the 3,4′-biphenylene bis[4-(4′-alkoxybenzoyloxy)]benzoate series the asymmetric nature originates from the 3,4′-substitution of the central biphenyl group and from the difference in length of the two terminal chains. All the melting points of the asymmetrical compounds in the series with the central phenyl unit are lower than those of the symmetrical compounds. The liquid crystalline B_1 or B_2 phase was retained in all cases. In the series with the central biphenyl unit the compounds with the shortest chain attached to the *para*-position of the central biphenyl unit have the lowest melting points. A significant lowering of the melting points in comparison with the symmetrically substituted compounds, however, could not be achieved. All the compounds of both series show a layer spacing which is comparable to those of the symmetrically substituted parent compounds. The observed switching behaviour of both the symmetric and asymmetric compounds with a B_2 phase was antiferroelectric.

1. Introduction

In 1996 Niori *et al.* [1] discovered that some non-chiral molecules with a bent or banana shape possess unusual and interesting physical properties. These banana-shaped compounds can form new smectic and two-dimensional ordered phases which are unlike those obtained from normal calamitic molecules [2]. These new phases are designated B_1–B_7 in order of their discovery. In recent years the number of new banana and sub-banana phases has risen dramatically. One of the most interesting banana mesophases is the B_2 phase in which the molecules are packed in layers and tilted with respect to the layer normal. The dipole moment arising from the bent shape of the molecules does not coincide with the layer normal and the tilt direction, thus giving rise to chiral domains. Current response measurements of the compounds which exhibit the B_2 phase gave evidence that the ground state is in most cases, antiferroelectric ($SmCP_A$) [3].

The fact that these non-chiral bent-core molecules exhibit antiferroelectric switching properties makes them very interesting for potential use in optical devices. Over the last 7 years numerous series of banana-shaped compounds have been synthesized and investigated. In general four parts of the banana-shaped molecules have been varied to study the influence of structure variations on mesomorphic properties and transitions temperatures. (1) The central part of the molecule: most of these compounds are composed of resorcinol derivatives substituted at the 1- and 3-positions. The 3,4′-disubstituted biphenyl central unit has proved also to be a suitable building block for obtaining banana-shaped molecules [4]. Several attempts to introduce new central units in banana-shaped compounds have been made previously but few of these compounds exhibit the desired B-phases [5]; recently, naphthalene-2,7-diol was introduced as a new type of central unit [6, 7]. Another way to obtain molecules with a bent shape is by the introduction of a central alkylene chain with an odd number of flexible units between two mesogenic units [8, 9], although compounds with these structures do not give banana phases as often as compounds with a central aromatic part. (2) The nature, position and direction of the linking groups. Ester [10] and a combination of ester and imine groups [11] are the most commonly used linking groups; by introducing different linking

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Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2004 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290410001724755

groups in each wing of the molecule, asymmetric banana-shaped compounds may be obtained [12]. (3) By varying the length [13] and nature [4] of the terminal alkyl(oxy) chains. (4) Introduction of lateral substituents to one of the aromatic rings of the banana-shaped compound [14–16].

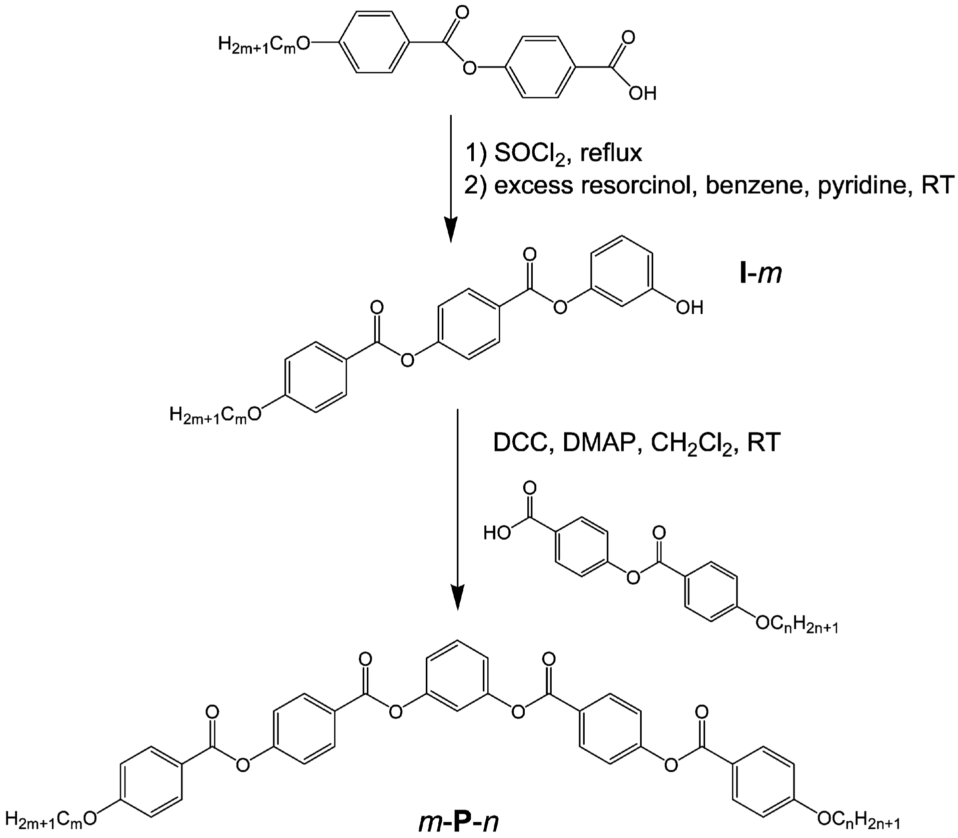
One reason for synthesizing different series of bent-core mesogens is to investigate whether changes in the structure might lower the melting points while retaining the desired liquid crystalline B-phase. In this paper we investigate two asymmetric series of banana-shaped compounds in which the lack of symmetry derives from differences in the terminal alkoxy chain lengths; in particular we study the effects of the asymmetry on the phase behaviour and phase transition temperatures. In the series *m*-**P**-*n* the central part of the molecule is a 1,3-disubstituted benzene; in the series *k*-**BP**-*l* the central part of the molecules is a 3,4′-disubstituted biphenyl. The asymmetric nature of the central part of the compounds in the *k*-**BP**-*l* series results in two different molecules for two given terminal chains. The shorter tail can be attached to either the *para*(4′)- or the *meta*(3)-position of the biphenyl group.

2. Experimental

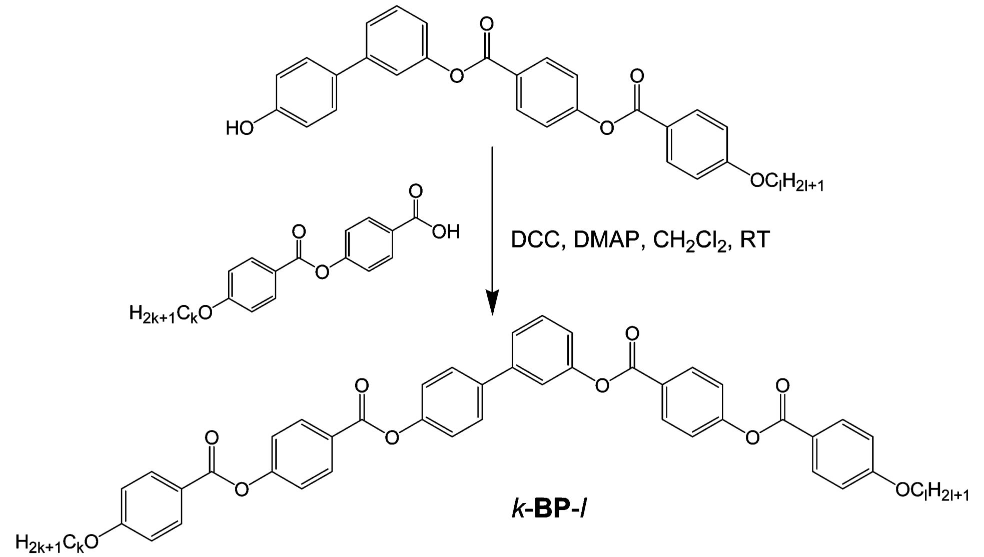
2.1. *Synthesis*

The compounds of series *m*-**P**-*n* were prepared according to scheme 1. The 4-(4-alkoxybenzoyloxy)benzoic acids were obtained by esterification of 4-alkoxybenzoyl chlorides with 4-hydroxybenzaldehyde [17] followed by $NaClO_2$ oxidation [18]. After conversion to the acid chloride with thionyl chloride, the first wing was attached to the central unit by reaction with excess resorcinol yielding compounds **I**-*m*. The second wing was attached via carbodiimide esterification [19] to yield the final compounds *m*-**P**-*n*. The symmetric compounds of the *m*-**P**-*n* series (*m* = *n*) were synthesized according to literature procedures [4].

The synthesis of the asymmetric compounds of the *k*-**BP**-*l* series is shown in scheme 2. The monosubstituted biphenol compounds (with one wing attached) were synthesized according to literature procedures [20]. The second wing was attached via the carbodiimide method [19] to yield the final compound. The symmetrically substituted compounds of the *k*-**BP**-*l* series (*k* = *l*) were synthesized according to literature procedures [4].



Scheme 1. Synthetic pathway used for the preparation of compounds *m*-**P**-*n*.



Scheme 2. Synthetic pathway used for the preparation of compounds *k*-**BP**-*l*.

2.1.1. *3-[4-(4-Dodecyloxybenzoyloxy)benzoyloxy]-phenol (**I**-12)*

4-(4-Dodecyloxybenzoyloxy)benzoic acid (0.90 g, 2.1 mmol) was heated under reflux in thionyl chloride (10 ml) for 2 h. Excess of thionyl chloride was removed by distillation under reduced pressure. The resulting acid chloride was dissolved in 10 ml dry benzene and added to a solution of 1.16 g (10.5 mmol) resorcinol in anhydrous pyridine (10 ml). The reaction mixture was stirred for 24 h at room temperature; it was then acidified with a 2 M HCl solution and extracted twice with CH_2Cl_2. The combined organic layers were washed with brine, then dried with Na_2SO_4 and filtered. The filtrate was concentrated and the residue purified by column chromotography (eluant: 1% MeOH in CH_2Cl_2); yield 55%, m.p. 125°C. ^1H NMR (200 MHz, $CDCl_3$) δ (ppm): 8.26 (d, 2H, Ar), 8.15 (d, 2H, Ar), 7.35 (d, 2H, Ar), 7.25 (m, 1H, Ar), 6.98 (d, 2H, Ar), 6.72 (m, 3H, Ar), 4.05 (t, 2H, OCH_2), 1.83 (m, 2H, $OCCH_2$), 1.60–1.27 (m, 18H, $9\times CH_2$), 0.88 (t, 3H, CH_3). ^{13}C NMR (200 MHz, $CDCl_3$) δ (ppm): 164.7, 164.5, 163.9, 156.7, 155.4, 151.7, 132.5, 131.9, 130.2, 126.8, 122.2, 120.8, 114.4, 113.8, 113.3, 109.4, 68.4, 31.9, 29.7, 29.6, 29.4, 29.1, 26.0, 22.7, 14.2. Elemental analysis for $C_{32}H_{38}O_6$ ($M=518.64$): calc. C 74.11, H 7.38; found C 74.25, H 7.40.

2.1.2. *1-[4-(4-Dodecyloxybenzoyloxy)benzoyloxy]-3-[4-(4-hexadecyloxybenzoyloxy)benzoyloxy]-benzene (12-**P**-16)*

To a mixture of 0.30 g (0.58 mmol) compound (**I**-12), 0.28 g (0.58 mmol) 4-(4-hexadecyloxybenzoyloxy)benzoic acid and a catalytic amount of 4-(*N*,*N*-dimethylamino)-pyridine (DMAP) in 15 ml CH_2Cl_2 was added 0.18 g (0.87 mmol) *N*,*N*-dicyclohexylcarbodiimide (DCC) in 5 ml CH_2Cl_2. This mixture was stirred for 24 h at room temperature under N_2. The precipitate was filtered off and washed with CH_2Cl_2. The filtrate was concentrated and the residue purified by column chromotography (eluant: 10% petroleum ether 40–60 in CH_2Cl_2). Finally, recrystallization from a mixture of petroleum ether 40–60 and CH_2Cl_2 gave colourless crystals; yield 68%. ^1H NMR (200 MHz, $CDCl_3$) δ (ppm): 8.28 (d, 4H, Ar), 8.15 (d, 4H, Ar), 7.48 (t, 1H, Ar), 7.39 (d, 4H, Ar), 7.20 (s + d, 3H, Ar), 6.98 (d, 4H, Ar), 4.05 (t, 4H, OCH_2), 1.84 (m, 4H, $OCCH_2$), 1.60–1.20 (m, 44H, $22\times CH_2$), 0.91 (t, 6H, CH_3). ^{13}C NMR (200 MHz, $CDCl_3$) δ (ppm): 164.1, 163.8, 155.5, 151.4, 132.5, 131.9, 129.9, 126.6, 122.2, 120.9, 119.3, 115.8, 114.4, 68.4, 31.9, 29.7, 29.6, 29.4, 29.1, 26.0, 22.7, 14.2. Elemental analysis for $C_{62}H_{78}O_{10}$ ($M=983.28$): calc. C 75.73, H 8.00; found C 76.01, H 8.16.

2.1.3. *3-[4-(4-Hexadecyloxybenzoyloxy)benzoyloxy]-4′-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]-biphenyl (12-**BP**-16)*

To a mixture of 0.20 g (0.31 mmol) 3-[4-(4-hexadecyloxybenzoyloxy)benzoyloxy]-4′-hydroxybiphenyl, 0.13 g (0.31 mmol) 4-(4-dodecyloxybenzoyloxy)benzoic acid and a catalytic amount of DMAP in 15 ml CH_2Cl_2, 0.10 g (0.49 mmol) DCC in 5 ml of CH_2Cl_2 was added. This mixture was stirred for 24 h at room temperature under N_2. The precipitate was filtered off and washed with CH_2Cl_2. The filtrate was concentrated and the residue purified by column chromotography (eluant: 10% petroleum ether 40–60 in CH_2Cl_2). Finally, recrystallization from a mixture of petroleum ether 40–60 and CH_2Cl_2 gave colourless crystals; yield 65%. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 8.30 (dd, 4H, Ar), 8.15 (d, 4H, Ar), 7.70–7.20 (m, 12H, Ar), 6.98 (d, 4H, Ar), 4.05 (t, 4H, OCH_2), 1.82 (m, 4H, $OCCH_2$), 1.45–1.10 (m, 44H, $22\times CH_2$), 0.88 (t, 6H, CH_3). ^{13}C NMR (200 MHz, $CDCl_3$) δ (ppm): 164.4, 163.8, 155.4, 151.3, 150.6, 142.1, 138.0, 132.5, 131.9, 129.9, 128.4, 126.8, 124.7, 122.2, 120.9, 120.5, 114.4, 68.4, 31.9, 29.7, 29.6, 29.4, 29.1, 26.0, 22.7, 14.2. HRMS calcd for $C_{68}H_{82}O_{10}$ 1058.5908; found 1058.5908.

2.2. *Characterization*

Melting points, phase transition temperatures and optical inspection of the liquid crystalline phases were determined on samples between ordinary glass slides using an Olympus BH-2 polarizing optical microscope equipped with a Mettler FP82HT hot stage, which was controlled by a Mettler FP80HT central processor. Differential scanning calorimetry (DSC) thermograms were obtained on a Perkin-Elmer DSC-7 system using 2–5 mg samples in 50 μl sample pans and a scan rate of 5°C min^{-1}. Temperature-dependent X-ray diffraction (XRD) patterns were measured on a Philips X'pert Pro MRD machine equipped with an Anton Paar camera for temperature control. For the measurements in the small angle region the sample was spread in the isotropic or the liquid crystalline phase on a thin glass slide (about 15 μm thick) which was placed on a temperature-regulated flat copper sample stage. This sample preparation sometimes caused a preferential planar orientation of the molecules in the liquid crystalline state. Current response measurements were performed on 6 μm thick polyimide-coated ITO cells with a measuring area of 0.36 cm^2 by applying a triangular voltage.

3. Results and discussion

3.1. *1,3-Phenylene compounds m-**P**-n*

The transition temperatures and corresponding enthalpies of the compounds of series *m*-**P**-*n* are summarized in table 1. The transition temperatures of three symmetrical compounds of the *m*-**P**-*n* series ($m=n$) are also presented in this table. The transition temperatures of these symmetrical compounds (8-**P**-8, 12-**P**-12 and 16-**P**-16) agree reasonably well with some recently published values [10, 21]. All members of the *m*-**P**-*n* series show liquid crystalline properties and all are enantiotropic with the exception of compound 8-**P**-12. In figure 1 the mesomorphic properties of the *m*-**P**-*n* series are represented schematically.

Table 1. Transition temperatures (°C), transition enthalpies (kJ mol^{-1}, in square brackets) and layer spacings *d* of the *m*-**P**-*n* series.

Compound	Cr		B_1		B_2		I	*d*/Å
8-**P**-8	●	121 [57]	●	121^a			●	
12-**P**-12	●	104 [42]			●	115 [22]	●	36.1
16-**P**-16	●	108 [57]			●	120 [25]	●	40.7
8-**P**-11	●	104 [42]	●	107^a			●	
8-**P**-12	●	103 [37]	(●	102.5)^a			●	
11-**P**-12	●	99 [37]			●	113 [21]	●	35.5
8-**P**-16	●	91 [33]			●	107 [19]	●	36.3
11-**P**-16	●	90 [38]			●	115 [22]	●	38.1
12-**P**-16	●	92 [41]			●	115 [23]	●	38.5

^{a}Could not be determined.

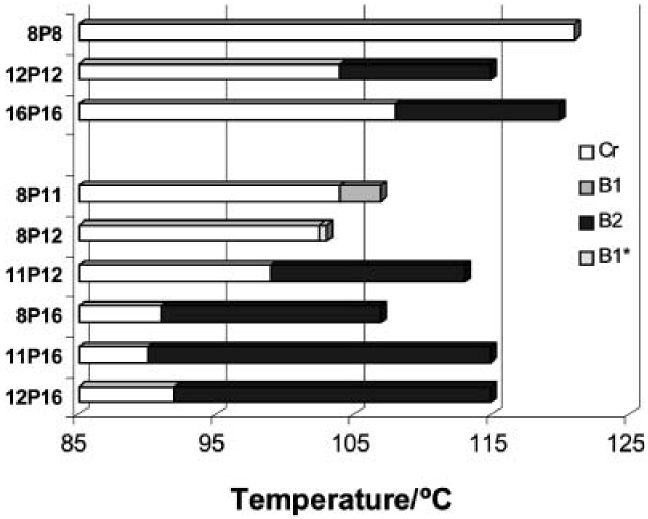


Figure 1. Graphical representation of the phase transition temperatures of compounds *m*-**P**-*n* (*monotropic B_1 phase).

On increasing the terminal chain lengths, the three symmetrical compounds show the trend anticipated for banana-shaped compounds. The short homologue 8-**P**-8 exhibits the columnar banana phase (B_1). This phase can be detected on cooling from the isotropic state by the formation of a mosaic-like texture. For this phase a rectangular columnar structure has been proposed [22]. The XRD pattern for this compound shows a broad peak in the wide angle region and two reflections in the small angle region. From these reflections the lattice parameters $a=30.3$ Å and $c=41.6$ Å were calculated. This indicates the presence of ~five molecules per unit cell or 2.5 (two or three) molecules per building block. As found in several other homologous series of banana-shaped compounds, the longer homologues of the *m*-**P**-*n* series (12-**P**-12 and 16-**P**-16) exhibit the $SmCP_A$ (B_2) mesophase. The textures which were observed for these compounds on cooling from the isotropic phase showed similarities with the textures found for other compounds with B_2 phases [2]. The XRD patterns for these compounds show first and second order layer reflections which point to a smectic phase. The broad peak in the wide angle region proves the liquid-like order of the molecules within the layers. The layer periodicities are given in table 1. According to Shen *et al.* [4] the B_1 phase is stable only if a partial overlap of the aromatic cores is possible. The B_2 phase can be obtained only if sufficiently long and flexible chains are present, which can suppress the formation of the frustrated B_1 structure. The critical terminal chain length for obtaining the B_2 phase increases with the size of the rigid aromatic core of the molecules.

In the *m*-**P**-*n* series, six compounds with two different terminal chain lengths were studied. For 8-**P**-11 and 8-**P**-12 a mosaic-like texture was observed on cooling from the isotropic state, which is characteristic of the columnar B_1 phase. Both compounds have a lower melting point than the symmetrical compound which also exhibits the B_1 phase (8-**P**-8).

The asymmetric compound 8-**P**-12 has a monotropic liquid crystal phase. The total number of carbon atoms in the terminal chains of 8-**P**-12 is 20. To determine the influence of asymmetry we have compared this compound with the symmetric compound 10-**P**-10 [10, 21] which also has 20 C-atoms in its terminal chains. Although both compounds have 20 carbon atoms in their terminal chains, their liquid crystalline properties are completely different. Symmetric compound 10-**P**-10 exhibits the B_2 mesophase while the asymmetric compound 8-**P**-12 exhibits the B_1 phase. It must be noted however that according to [21] compound 10-**P**-10 shows coexisting B_1 and B_2 phases over a small temperature range. Apparently the thermotropic properties of this series of compounds is not determined solely by the total number of C-atoms in the terminal chains. As proposed by Shen *et al.* [4] the long terminal chains in 10-**P**-10 prevent partial overlap between the aromatic bent cores of the antiparallel arranged molecules and hence the B_1 phase is suppressed. For compound 8-**P**-12 formation of the B_1 phase is still favoured over the formation of a layered structure such as the B_2 phase. Apparently asymmetry in banana-shaped compounds, by introducing two different terminal tail lengths, destabilizes the B_2 phase.

The compounds with the longer terminal chains 11-**P**-12, 8-**P**-16, 11-**P**-16 and 12-**P**-16 all exhibit the B_2 mesophase. On cooling, the optical textures of these compounds show small coloured domains with some fans, but also schlieren textures were observed. This is typical for B_2 textures as was also observed in several other B_2 compounds [2]. Figure 2 shows the electric response of compound 12-**P**-16 under a triangular wave voltage. Two peaks were recorded during a half period indicating antiferroelectric switching behaviour. The spontaneous polarization determined by integration of the switching current peaks was 870 nC cm^{-1}.

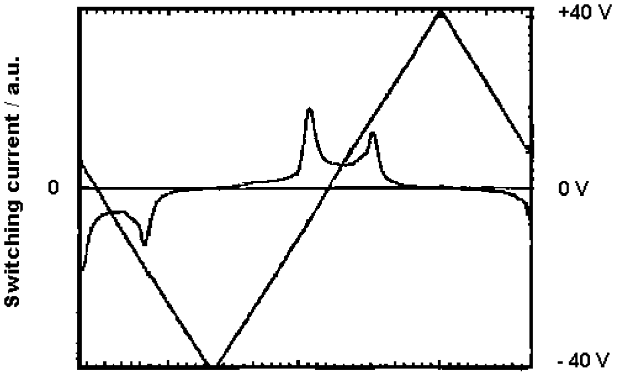


Figure 2. Switching current response (a.u.) obtained in the B_2 phase of compound 12-**P**-16 at 106°C by applying a triangular voltage (50 Hz).

Asymmetric materials usually have a broader mesophase range than their symmetric analogues [23, 24]. From table 1 and figure 1 it can indeed be seen that the compounds with two different terminal alkoxy tails have the broader mesophase ranges. This is caused by a lowering of the melting points. For this series of compounds a difference in length of the terminal chains of five or six carbon atoms is probably required to make the lowering of the melting points as large as possible.

The X-ray patterns of planar oriented samples exhibiting the B_2 phase all indicate a tilted smectic phase in which the layer spacing *d* steadily increases with the total number of C-atoms (table 1). Figure 3

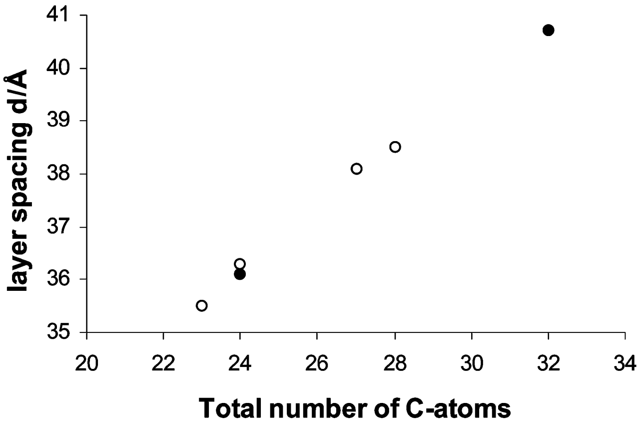


Figure 3. Dependence of the layer spacings *d* of the symmetric and asymmetric compounds of the *m*-**P**-*n* series on the total number of C-atoms in the terminal chains ($m=n$, ●; $m \neq n$, ○).

shows the relationship between the total number of C-atoms in the terminal alkyl chains of these compounds and the layer spacing. The linear relationship shows that in all cases the layer organizations (tilt angle) for the symmetric and asymmetric compounds are very similar. For all compounds in the *m*-**P**-*n* series that exhibit the B_2 mesophase, a tilt angle of approximately 45° was calculated from the molecular lengths (assuming a bending angle of 120°) and the layer spacings *d*. This tilt angle was also observed in other compounds possessing the B_2 phase [4, 25].

3.2. *3,4′-Biphenyl compounds k-**BP**-l*

To investigate further the influence of two different terminal chains, we synthesized a second series of compounds in which the central phenyl group of the *m*-**P**-*n* series is replaced by a biphenyl group. The bent shape of the molecules in the *k*-**BP**-*l* series is caused by the 3,4′-disubstitution of the central biphenyl unit. The thermotropic properties of the symmetrically substituted compounds with terminal chains ranging from 8 to 14 have been described by Shen *et al.* [4]. We have synthesized and studied three symmetrically substituted compounds ($k=l=8$, 12 and 16), and seven asymmetrically substituted compounds with different combinations of terminal chain lengths. The transition temperatures together with the associated transition enthalpies of the compounds of series *k*-**BP**-*l* are given in table 2. All melting points are determined on the first heating. It must be noted that in some cases melting points are significantly lower on second and third heating.

The mesomorphic properties of the compounds of series *k*-**BP**-*l* (and also of the parent compounds 8-**BP**-8, 12-**BP**-12 and 16-**BP**-16) are represented schematically in figure 4. Replacement of the 1,3-disubstituted resorcinol unit in the *m*-**P**-*n* series with the 3,4′-disubstituted biphenyl in the *k*-**BP**-*l* series results, for the symmetrically substituted compounds, in an increase of the liquid crystalline range. All three parent compounds retain their liquid crystalline mesophase on increasing the size of the rigid core of the molecule. As predicted by Shen *et al.* [4] the transition from the columnar B_1 phase to the switchable B_2 phase occurs in the **P**-series at 9-**P**-9 to 10-**P**-10 [10] and in the **BP**-series at 11-**BP**-11 to 12-**BP**-12 due to the increase in size of the rigid core.

Table 2. Transition temperatures (°C), transition enthalpies (kJ mol^{-1}, in square brackets) and layer spacings *d* of the *k*-**BP**-*l* series.

Compound	Cr		B_1		B_2		I	*d*/Å
8-**BP**-8	●	132 [25]	●	176 [20]			●	
12-**BP**-12	●	109 [38]			●	157 [23]	●	38.9
16-**BP**-16	●	91 [52]			●	160 [27]	●	43.8
8-**BP**-12	●	105 [29]	●	164 [20]			●	
12-**BP**-8	●	113 [56]	●	157 [19]			●	
8-**BP**-16	●	112[a]			●	149 [21]	●	39.4
16-**BP**-8	●	116 [62]			●	149 [20]	●	39.7
12-**BP**-16	●	99[a]			●	158 [25]	●	41.6
16-**BP**-12	●	109 [42]			●	157 [24]	●	41.6
11-**BP**-12	●	105 [35]			●	156 [24]	●	38.4

[a] Could not be determined.

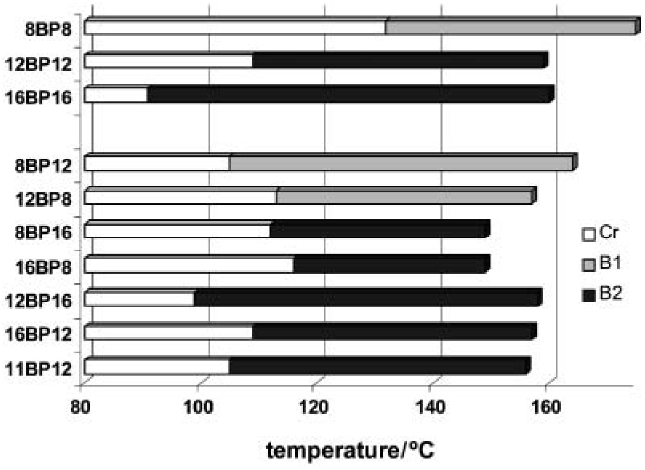
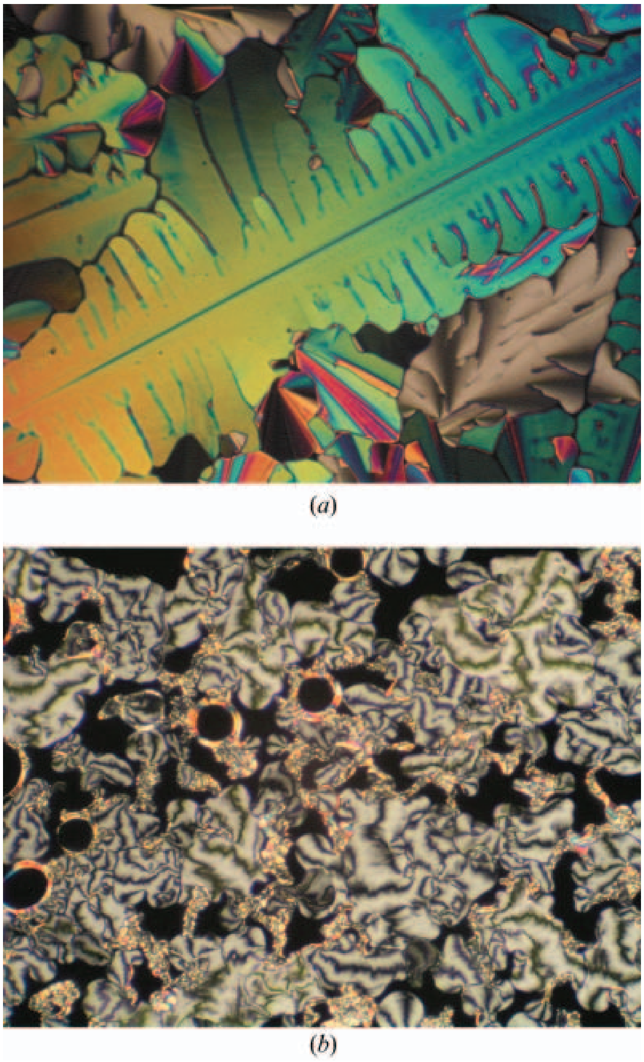


Figure 4. Graphical representation of the phase transition temperatures of compounds *k*-**BP**-*l*.

We have studied three pairs of non-symmetrically substituted compounds in the *k*-**BP**-*l* series. The pair with the shortest chains (8-**BP**-12 and 12-**BP**-8) exhibit the B_1 phase while the other pairs show the B_2 phase. Figure 5 shows an optical photomicrograph of the B_1 texture obtained for compound 12-**BP**-8 and the schlieren pattern obtained for the B_2 mesophase of compound 12-**BP**-16. For all three pairs the compounds with the shortest chain attached to the *para*-position of the biphenyl group have the lowest melting points. A lowering of the melting point could however not be achieved by asymmetric substitution of the **BP**-compounds when compared with those of the symmetrically substituted **BP**-compounds.

Asymmetric molecules usually have a broader mesophase range than their symmetric analogues mainly due to a lowering of the melting points. According to Mieczkowski *et al.* [24] this also has a strong influence on the polar structure of the mesophase; asymmetric compounds have a tendency to form ferroelectric phases instead of antiferroelectric phases. In both the **P**- and **BP**-series the switching behaviour was antiferroelectric as was also found in the symmetrically substituted compounds [10]. In the **BP**-series we have studied mainly compounds which differ by four or eight C-atoms in their terminal tails. To investigate whether a smaller difference in length of the terminal



(*a*)

(*b*)

Figure 5. Optical photomicrographs of the textures observed on cooling from the isotropic state at 155°C for (*a*) B_1 phase of compound 12-**BP**-8 and (*b*) B_2 phase of compound 12-**BP**-16.

chains will result in a lower melting point we have also synthesized compound 11-**BP**-12 (B_2 phase). When compared with 12-**BP**-12 the melting point has decreased by 4 to 105°C which suggests that for the compounds in the *k*-**BP**-*l* series, only a small difference in the number of C-atoms in the terminal chains is effective in lowering the melting point.

The X-ray patterns of all compounds of the *k*-**BP**-*l* series show a diffuse wide angle peak. The compounds which exhibit the B_1 phase all show two reflections in the small angle region pointing to the existence of a two-dimensional rectangular cell. From the cell dimensions the number of molecules per building block can be calculated [26]. It was found to increase from ~2.5 for 8-**BP**-8 to ~3 for 8-**BP**-12 and 12-**BP**-8. The layer spacings *d* of the compounds with a B_2 phase are listed in table 2 and shown in figure 6. Again it seems that there is barely any change in layer organization due to the introduction of two different terminal alkyl chains. For all compounds there is a linear relationship between the total number of C-atoms in the terminal chains, and the layer spacing *d*. In all cases the tilt angle of the molecules in the smectic layers is ~45° (assuming a bending angle of 120°). It has to be noted, however, that the layer spacings for the compounds with the largest asymmetric component (8-**BP**-16 and 16-**BP**-8) are slightly larger than the expected layer spacing for symmetrically substituted compounds.

4. Conclusions

Two series of asymmetrical ester-like banana-shaped compounds with different terminal chain lengths have been synthesized and studied. Going from the symmetrical *m*-**P**-*n* series with a central phenyl group to the symmetrically substituted *k*-**BP**-*l* series with a central biphenyl group, the liquid crystalline range increases dramatically with retention of the liquid crystalline B-phases. For the asymmetrical compounds of the **P**-series the melting points are lower when compared with those of the parent compounds. To most effectively lower the melting points for this series of compounds a difference in terminal chain length of ~5 C-atoms (11-**P**-16) is required.

For the compounds of the **BP**-series it seems more difficult to lower the melting points. Since all compounds (also compounds with $k=l$) of the **BP**-series have an asymmetric central part it is difficult to introduce even more asymmetry to lower the melting points. A small difference in terminal chain length

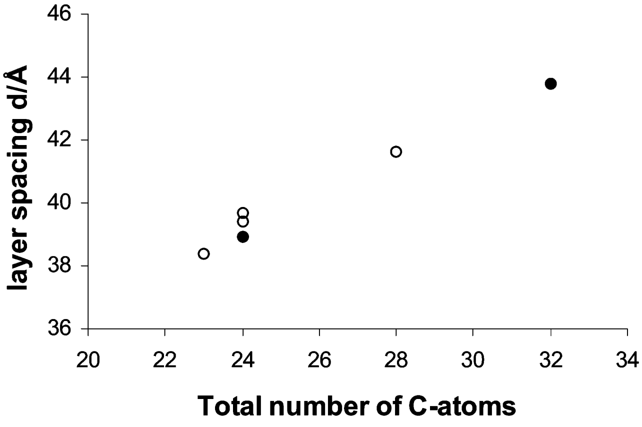


Figure 6. Dependence of the layer spacings *d* of the symmetrically substituted compounds and non-symmetric compounds of the *k*-**BP**-*l* series on the total number of C-atoms in the terminal chains ($k=l$, ●; $k \neq l$, ○).

however (11-**BP**-12) can result in a small reduction of the melting point. Surprisingly, the asymmetrically substituted compounds in the *k*-**BP**-*l* series with $k<l$ (shortest terminal chain attached to the *para*-position of the central biphenyl group) give the lowest melting points.

This study has shown that the introduction of two different terminal alkyl chains can lower the melting points of banana-shaped compounds that exhibit the switchable B_2 phase. This method seems only effective, however, when the central part of the molecule is itself symmetric.

Mr E. van der Klift is thanked for performing elemental analyses, Mr A. Verhulst (Philips) for electro-optical measurements and Dr M. A. Posthumus for HRMS. This work was financially supported by the Dutch Technology Foundation (STW).

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