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Liquid Crystals

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Non-symmetric bent-core mesogens with one terminal vinyl group

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Two series of non-symmetric banana-shaped compounds, both with one alkyl and one alkenyl terminal tail, have been synthesized and studied. Both series were compared with the corresponding series with two saturated terminal alkyl tails. All the compounds have a bent central 1,3-phenylene bis(4-benzoyloxy)benzoate core; their mesophases were characterized by polarizing optical microscopy, differential scanning calorimetry, X-ray diffraction and switching current response experiments. In all four series one of the terminal tails is varied from OC_8H_{17} to $OC_{16}H_{33}$. The other terminal tails are $OC_{11}H_{23}$, $O(CH_2)_9CH{=}CH_2$, $OC_{10}H_{21}$ and $O(CH_2)_8CH{=}CH_2$. The short-tailed compounds show monotropic or enantiotropic B_1 phases and the long-tailed compounds the B_2 phase. The introduction of one terminal vinyl group slightly lowers the transition temperatures. The introduction of a second terminal vinyl group further suppresses the liquid crystalline properties. All compounds with B_2 phases have layer spacings that suggest a tilt of ~45° of the bent molecules in the layers, and their switching behaviour is antiferroelectric.

1. Introduction

Ferroelectricity [1] and antiferroelectricity [2] were first discovered in chiral tilted smectic phases. In 1996 Niori *et al.*[3] were the first to report smectic phases of achiral molecules with a bent core which had ferroelectric switching properties. Ever since, these so-called banana-shaped liquid crystals have attracted great interest [4, 5]. Among the eight B phases (B_1–B_8) known to date [4, 6] the B_2 phase is the most interesting. In this B_2 phase the molecules are ordered in a layered arrangement (Sm) in which the bent molecules are tilted (C) and the dipoles point along a common direction within the layer (P); therefore this phase is also designated as a SmCP phase. The ground state is mainly regarded as antiferroelectric [7], although ferroelectric ground states have also been reported [8].

In the past eight years several hundred banana-shaped compounds have been synthesized and studied [4, 9–12]. It is however still very difficult to establish structure–property relationships for this kind of compound. Most bent-core molecules studied so far in the literature are symmetric. Some compounds, however, lack an internal mirror plane and are therefore referred to as asymmetric or non-symmetric. When using the term 'asymmetry' this should not be confused with 'chirality'. Non-symmetry for banana-shaped compounds can and has been achieved in a number of ways: (1) by a non-symmetrically substituted central group [9, 13–17]; (2) by two different terminal end groups or chains [18–28]; (3) by different linking groups in each wing of the molecule [19, 23, 28]; (4) by different (polar) substituents in each wing of the molecule [20–22, 26]. In most of these cases, however, the non-symmetric nature of the investigated compounds arises from a combination of two of these possibilities.

In a previous study [27] we investigated the influence of non-symmetry in a series of banana-shaped compounds with two terminal alkoxy tails of different length. In the present study we have extended the number of compounds in this *m*-**P**-*n* series, but have also synthesized and studied compounds with one or two terminal alkene bonds. These compounds may be interesting for preparing oligomeric or polymeric siloxanes by a hydrosilylation reaction. Four homologous series, each consisting of six compounds have been studied (scheme 1). In the *m*-**P**-11 and *m*-**P**-10 series the lack of symmetry is derived solely from the difference in length of the two terminal alkoxy tails. In series *m*-**P**-11a and *m*-**P**-10a the lack of symmetry is derived from the difference in length of the two terminal tails and the presence of one terminal vinyl group.

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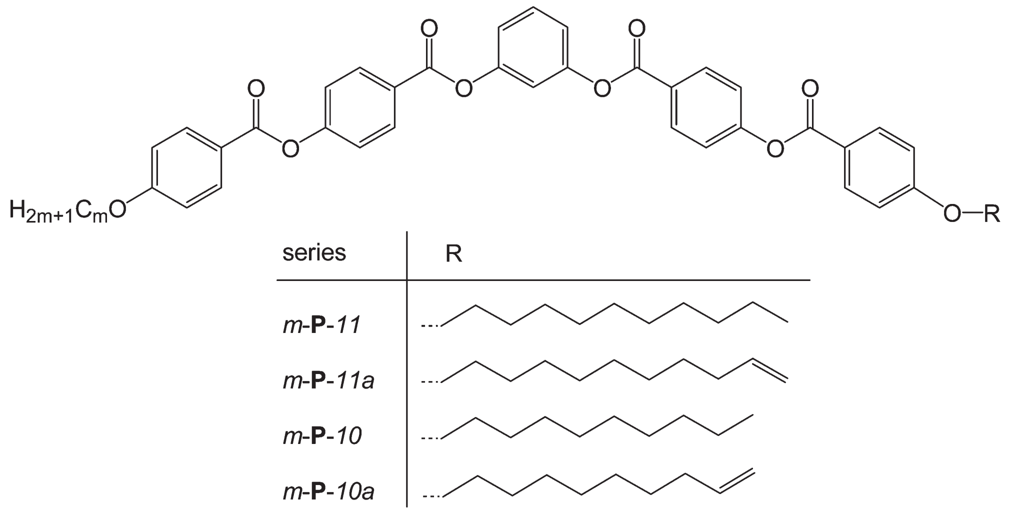


Scheme 1. General structures of the four homologous series.

2. Experimental

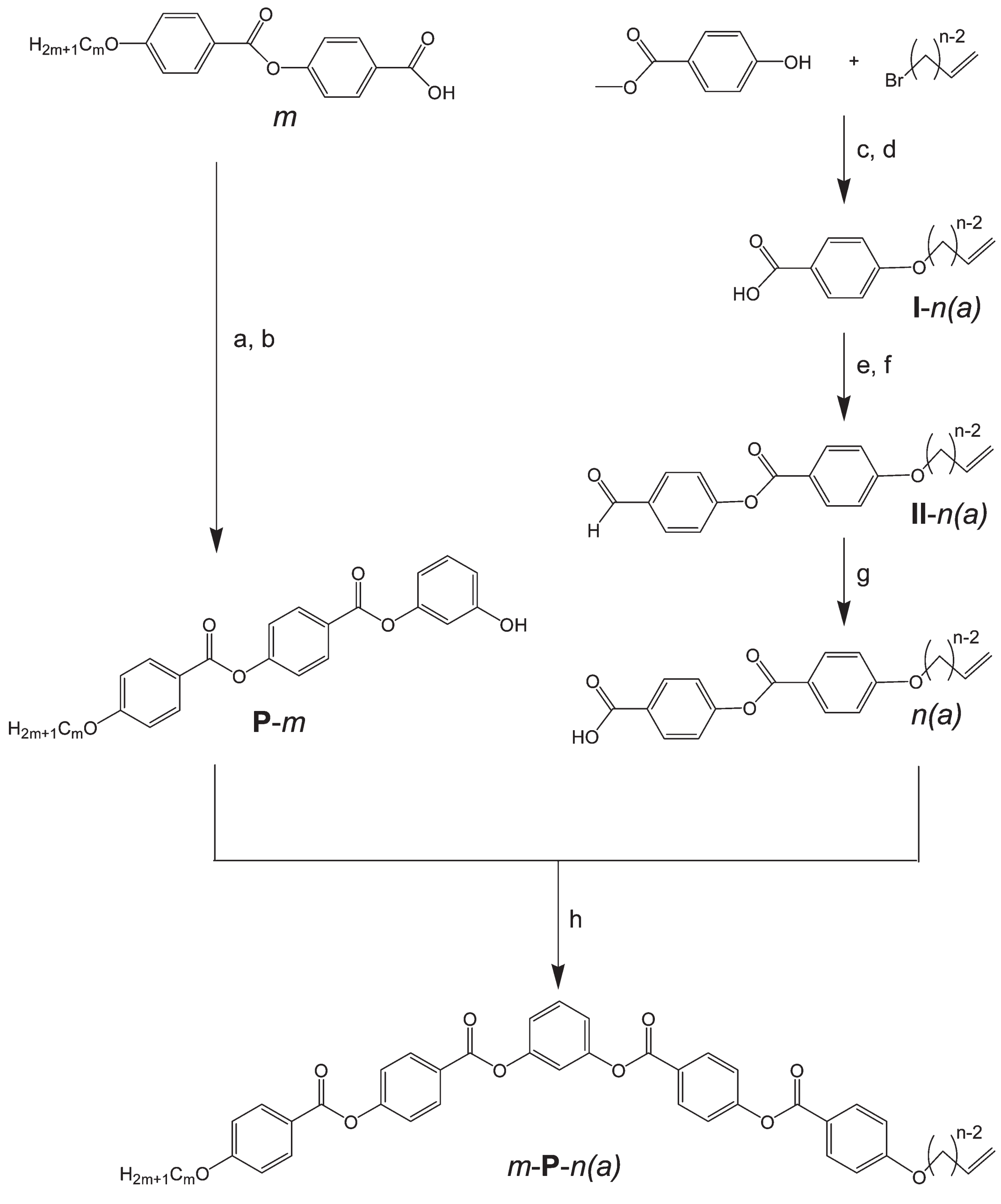
2.1. *Synthesis*

The compounds of series *m*-**P**-*n* (with no terminal double bonds present) were prepared according to literature procedures [27]. The compounds of series *m*-**P**-*n*(a) were prepared according to scheme 2. Monosubstituted resorcinol derivatives **P**-*m* were obtained by first converting the 4-(4-alkyloxybenzoyloxy)benzoic acid (*m*) with thionyl chloride to the acid chlorides, and subsequent reaction with excess resorcinol. Compounds **I**-*n*(a) were obtained by etherification of the corresponding bromoalkene (n=10 and 11) with methyl 4-hydroxybenzoate with K_2CO_3 as base, followed by hydrolysis with KOH. Compounds *n*(a) were obtained by esterification of the acid chlorides of **I**-*n*(a) with 4-hydroxybenzaldehyde, **II**-*n*(a), followed by $NaClO_2$ oxidation [29]. End products *m*-**P**-*n*(a) were obtained via carbodiimide esterification of **P**-*m* and *n*(a) [30].

2.1.1. 4-[4-(9-Decenyloxy)benzoyloxy]benzaldehyde (II-**10a).** Compound **I**-10a (4.50 g, 16.3 mmol) was heated under reflux in thionyl chloride (30 ml) for 2 h. Excess thionyl chloride was removed by destillation under reduced pressure. The resulting acid chloride was dissolved in 15 ml dry toluene and added to a solution of 2.07 g (17.0 mmol) 4-hydroxybenzaldehyde in a mixture of 20 ml pyridine and 15 ml toluene. The reaction mixture was stirred for 24 h at room temperature; it was then acidified with a 2M 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 chromatography (eluant CH_2Cl_2); yield 95%, Cr 64°C (N 51°C) I. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 10.02 (s, 1H, CHO), 8.14 (d, 2H, Ar), 7.96 (d, 2H, Ar), 7.39 (d, 2H, Ar), 6.98 (d, 2H, Ar), 5.81 (m, 1H, =CH), 4.98 (m, 2H, $=CH_2$), 4.04 (t, 2H, OCH_2), 2.02 (m, 2H, $=CCH_2$), 1.82 (m, 2H, $OCCH_2$) 1.60–1.33 (m, 10H, $5 \times CH_2$). ^{13}C NMR ($CDCl_3$) δ (ppm): 191.1, 164.3, 163.9, 155.9, 139.2, 133.9, 132.5, 131.3, 122.6, 120.8, 114.4, 114.2, 68.4, 33.8, 29.4, 29.3, 29.1, 28.9, 26.0.

2.1.2. 4-[4-(9-Decenyloxy)benzoyloxy]benzoic acid (10a). Compound **II**-10a (5.90 g, 15.5 mmol) and resorcinol (2.20 g) were dissolved in *tert*-butyl alcohol (300 ml). To this solution was added dropwise, over 10 min, a solution of sodium chlorite (80%, Aldrich) (8.10 g, 89.6 mmol) and sodium dihydrogenphosphate monohydrate (6.42 g, 46.5 mmol) in 85 ml water. The resulting pale yellow reaction mixture was then stirred at room temperature overnight. Volatile components were removed *in vacuo* and the residue was dissolved in 250 ml water. The aqueous solution was acidified to pH 3 by adding 1M HCl. The white precipitate was filtered, washed successively with water and hexane, and dried in the air; yield 87%, Cr 114 SmC 180 N 220 I (°C). ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 8.17 (dd, 4H, Ar), 7.33 (d, 2H, Ar), 6.98 (d, 2H, Ar), 5.82 (m, 1H, =CH), 4.98 (m, 2H, $=CH_2$), 4.04 (t, 2H, OCH_2), 2.02 (m, 2H, $=CCH_2$), 1.82 (m, 2H, $OCCH_2$) 1.60–1.34 (m, 10H, $5 \times CH_2$). ^{13}C NMR ($CDCl_3$) δ (ppm): 171.5, 164.4, 163.8, 155.6, 139.2, 132.4, 131.9, 126.7, 122.0, 120.9, 114.4, 114.2, 68.4, 33.8, 29.4, 29.3, 29.1, 28.9, 26.0.

2.1.3. 1-{4-[4-(10-Undecenyloxy)benzoyloxy]benzoyloxy}-3-[4-(4-octyloxybenzoyloxy)benzoyloxy]benzene (8-P**-11a).** To a mixture of 0.46 g (1.0 mmol) 3-[4-(4-octyloxybenzoyloxy)benzoyloxy]phenol (**P**-8) 0.41 g



Scheme 2. Synthesis of compounds *m*-**P**-*n*(a): a) $SOCl_2$, reflux; b) excess resorcinol, toluene, pyridine, rt; c) K_2CO_3, butanone, reflux; d) KOH, EtOH, reflux; e) $SOCl_2$, reflux; f) 4-hydroxybenzaldehyde, toluene, pyridine, rt; g) $NaClO_2$, resorcinol, NaH_2PO_4, *t*-BuOH, H_2O, rt [29]; h) DCC, DMAP, CH_2Cl_2, rt.

(1.0 mmol) 4-[4-(10-undecenyloxy)benzoyloxy]benzoic acid, and a catalytic amount of 4-(*N*,*N*-dimethylamino)pyridine (DMAP) in 25 ml CH_2Cl_2 was added 0.31 g (1.5 mmol) *N*,*N*-dicyclohexylcarbodiimide (DCC) in 10 ml of 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 chromatography (eluant CH_2Cl_2). Finally, recrystallization from a mixture of petroleum-ether 40–60 and CH_2Cl_2 gave colourless crystals; yield 64 %. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 8.28 (d, 4H, Ar), 8.16 (d, 4H, Ar), 7.50 (t, 1H, Ar), 7.38 (d, 4H, Ar), 7.19 (s+d, 3H, Ar), 7.00 (d, 4H, Ar), 5.81 (m, 1H, $=CH$), 4.96 (m, 2H, $=CH_2$), 4.05 (t, 4H, OCH_2), 2.03 (m, 2H, $C=CCH_2$), 1.79 (m, 4H, $OCCH_2$), 1.55–1.32 (m, 22H, $11 \times CH_2$), 0.90 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ (ppm): 164.3 164.1, 163.8, 155.5, 151.4, 139.2, 132.5, 131.9, 129.9, 126.6, 122.2, 120.9, 119.3, 115.9, 114.4, 114.2, 68.4, 33.8, 31.8, 29.5, 29.4, 29.3, 29.1, 28.9, 26.0, 22.7, 14.1. Elemental analysis for $C_{53}H_{58}O_{10}$ (M=855.04): calc. C 74.45, H 6.84; found C 74.74, H 6.92%. HRMS calc. for $C_{53}H_{58}O_{10}$ 854.4030; found 854.4013.

2.1.4. 1-[4-(4-Undecyloxybenzoyloxy)benzoyloxy]-3-[4-(4-octyloxybenzoyloxy)benzoyloxy]benzene (8-P-11). This compound was prepared similarly to 8-**P**-11a from 4-(4-undecyloxybenzoyloxy)benzoic acid (*m*=11) and **P**-8; yield 64 %.^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 8.27 (d, 4H, Ar), 8.14 (d, 4H, Ar), 7.49 (t, 1H, Ar), 7.36 (d, 4H, Ar), 7.18 (s+d, 3H, Ar), 6.98 (d, 4H, Ar), 4.05 (t, 4H, OCH_2), 1.78 (m, 4H, $OCCH_2$), 1.55–1.27 (m, 26H, $13\times CH_2$), 0.87 (t, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ (ppm): 164.3, 164.1, 163.8, 155.5, 151.4, 132.5, 131.9, 129.9, 126.6, 122.2, 120.9, 119.3, 115.9, 114.4, 68.4, 31.9, 31.8, 29.6, 29.4, 29.2, 29.1, 26.0, 22.7, 14.2. Elemental analysis for $C_{53}H_{60}O_{10}$ (*M*=857.05): calc. C 74.28, H 7.06; found C 74.44, H 7.10%.

2.1.5. 1-{4-[4-(9-Decenyloxy)benzoyloxy]benzoyloxy}-3-[4-(4-octyloxybenzoyloxy)benzoyloxy]benzene (8-P-10a). This compound was prepared similarly to 8-**P**-11a from compounds 10a and **P**-8; yield 68 %. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 8.28 (d, 4H, Ar), 8.16 (d, 4H, Ar), 7.50 (t, 1H, Ar), 7.38 (d, 4H, Ar), 7.19 (s+d, 3H, Ar), 6.99 (d, 4H, Ar), 5.81 (m, 1H, =CH), 4.97 (m, 2H, $=CH_2$), 4.05 (t, 4H, OCH_2), 2.04 (m, 2H, $C=CCH_2$), 1.83 (m, 4H, $OCCH_2$), 1.60–1.34 (m, 20H, $10\times CH_2$), 0.90 (t, 3H, CH_3). ^{13}C NMR (200 MHz, $CDCl_3$) δ (ppm): 164.3 164.1, 163.8, 155.5, 151.4, 139.2, 132.5, 131.9, 129.9, 126.6, 122.2, 120.9, 119.3, 115.9, 114.4, 114.2, 68.4, 33.8, 31.8, 29.4, 29.3, 29.1, 28.9, 26.0, 22.7, 14.2. Elemental analysis for $C_{52}H_{56}O_{10}$ (*M*=841.01): calc. C 74.26, H 6.71; found C 74.23, H 6.75%.

2.2. *Measurements*

Melting points, thermal phase transition temperatures and optical character of the liquid crystalline phases were determined on samples between ordinary glass slides using an Olympus BH-2 polarizing 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 2–4 mg samples in 50 µl sample pans and a scan rate of 5°C min^{-1}. ΔH is calculated in kJ mol^{-1}. Temperature-dependent X-ray curves were measured on a Philips X'pert Pro MRD machine equipped with an Anton Paar camera for temperature control. For measurements in the small angle region the sample was spread in the isotropic or 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. *m-P-11 and m-P-11a series*

In table 1 the phase transition temperatures and corresponding enthalpies of the compounds of series *m*-**P**-11 and *m*-**P**-11a are summarized. In the compounds of the *m*-**P**-11 series one of the terminal tails is $OC_{11}H_{23}$; the other is varied between OC_8H_{17} (*m*=8) and $OC_{16}H_{33}$ (*m*=16). In the compounds of the *m*-**P**-11a series one of the terminal tails is $O(CH_2)_9CH=CH_2$ (*11a*) and *m* is varied between 8 and 16.

Table 1. Transition temperatures (°C), transition enthalpies (kJ mol^{-1}, in brackets) and layer spacings *d* (Å) of the *m*-**P**-11 and *m*-**P**-11a series.

Compound	Cr	B_1	B_2	I	*d*
8-**P**-11[b]	• 104 (42)	• 107([a])		•	—
10-**P**-11	• 98 (34)		• 111 (20)	•	34.0
11-**P**-11[c,d]	• 104 (38)		• 113 (21)	•	34.9
12-**P**-11[b]	• 99 (37)		• 113 (21)	•	35.5
14-**P**-11	• 90 (35)		• 115 (22)	•	37.0
16-**P**-11[b]	• 90 (38)		• 115 (22)	•	38.1
8-**P**-11a	• 103 (37)	(• 100.5) (16)		•	—
10-**P**-11a	• 103 ([a])		• 104 (19)	•	33.8
11-**P**-11a	• 102 (29)		• 105 (18)	•	34.8
12-**P**-11a	• 91 (32)		• 103.5 (19)	•	35.4
14-**P**-11a	• 85 (35)		• 107 (21)	•	36.5
16-**P**-11a	• 84 (33)		• 107 (21)	•	38.1

[a] Could not be determined; [b] See ref [27]; [c] See ref [10]; [d] See ref [35].

The mesomorphic properties of the compounds in the *m*-**P**-11 series are represented schematically in figure 1. All compounds in this series show enantiotropic liquid crystalline B phases. Only compound 8-**P**-11 with one short OC_8H_{17} tail shows the columnar B_1 phase; all the other compounds in this series show the B_2 phase. The phase sequence B_1–B_2 with increasing terminal tail length is often observed in banana-shaped liquid crystals [9]. On increasing *m*, the isotropization temperatures of the compounds in series *m*-**P**-11 gradually increase from 107 to 115°C. The symmetric series (*m*-**P**-*m*; $m=1$–18) also shows a slight increase in the B_2–I transition temperatures with increasing *m* ($m=10$, $T_I=110$°C; $m=18$, $T_I=121.5$°C) [10]. The melting points of the compounds in the *m*-**P**-11 series decrease considerably with increasing *m*. This is caused by the increasing non-symmetric shape of the compounds with the largest *m*. Due to the symmetric shape of compound 11-**P**-11, a maximum in melting point for this compound was observed. In contrast to the non-symmetric *m*-**P**-11 series, the symmetric series [10] shows an increase of melting point with increasing tail length.

In table 1 and figure 2 the mesomorphic properties of the compounds of series *m*-**P**-11a are given. All long-tailed compounds ($m=10$–16) exhibit an enantiotropic B_2 mesophase. The compound with the shortest tail shows a monotropic columnar B_1 phase. Again the isotropization temperatures gradually increase and the melting points gradually decrease with increasing *m*. Hence the B_2 mesophase range increases with increasing *m*.

Figure 3 shows the electric response of compound 14-**P**-11a under a triangular wave voltage. Two peaks were recorded during a half period indicating antiferroelectric switching behaviour.

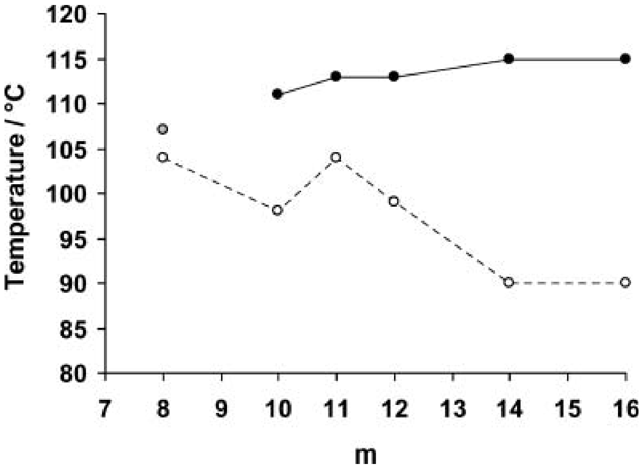


Figure 1. Dependence of the melting points (- -○- -), B_1–I transition (●) and B_2–I transitions (—●—) on *m* for series *m*-**P**-11.

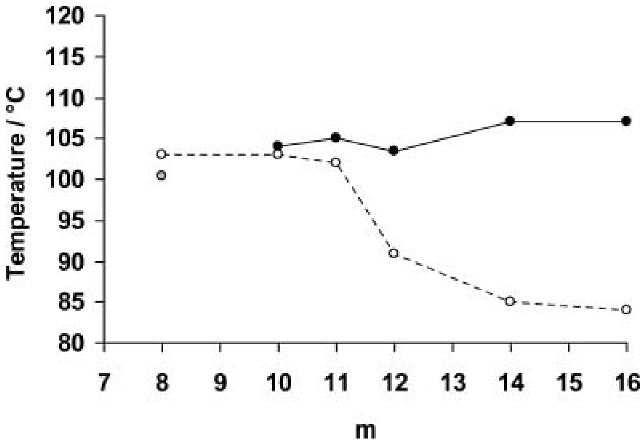


Figure 2. Dependence of the melting points (- -○- -), B_1–I transition (●) and B_2–I transitions (—●—) on *m* for series *m*-**P**-11a.

XRD measurements showed that all B_2 compounds in the *m*-**P**-11 and *m*-**P**-11a series have a sharp reflection in the small angle region corresponding to the layer spacing *d* (table 1). Sometimes second and third order reflections were also observed. The liquid-like order within the B_2 mesophase was demonstrated by a diffuse wide angle scattering. In all cases a tilt angle of the molecules in the smectic layers of ~45° was calculated (assuming a bending angle of 120°). As expected, the layer spacings *d* and tilt angle of the B_2 compounds in series *m*-**P**-11a are comparable with those of compounds in the *m*-**P**-11 series. Both series show a linear relation between *d* and *m*.

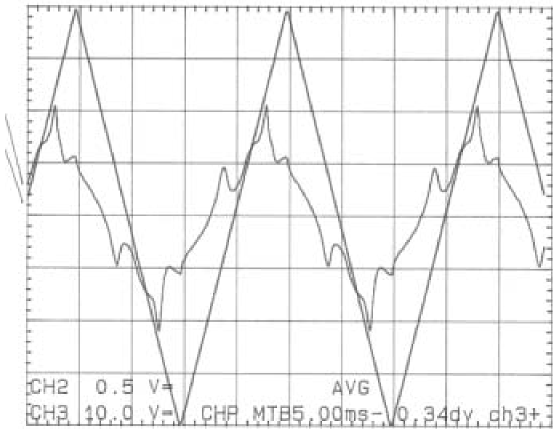


Figure 3. Switching current response (a.u.) obtained in the B_2 phase of compound 14-**P**-11a at 100°C by applying a triangular voltage of 50 Hz.

Table 2. Transition temperatures (°C), transition enthalpies (kJ mol^{-1}, in brackets) and layer spacings *d* (Å) of the *m*-**P**-10 and *m*-**P**-10a series.

Compound	Cr	B_1	B_2	I	*d*
8-**P**-10	• 106 (19)	• 111 (18)		•	—
10-**P**-10[b]	• 111 (53)		(• 110) (20)	•	33.7
11-**P**-10	• 98 (34)		• 111 (20)	•	34.0
12-**P**-10	• 92 (32)		• 111 (21)	•	34.6
14-**P**-10	• 89 (34)		• 112 (21)	•	35.7
16-**P**-10	• 88 (29)		• 112 (21)	•	37.1
8-**P**-10a	• 106 (36)	(• 103.5) (16)		•	—
10-**P**-10a	• 107 (61)	(• 101.5) (18)		•	—
11-**P**-10a	• 102 ([a])		• 102 ([a])	•	33.8
12-**P**-10a	• 98 (15)		• 102 (16)	•	34.8
14-**P**-10a	• 82 (18)		• 104 (19)	•	35.7
16-**P**-10a	• 82 (7)		• 104 (19)	•	37.4

[a] Could not be determined; [b] See refs [9, 10, 35].

3.2. *m-P-10 and m-P-10a series*

The phase transition temperatures and associated enthalpy values for the compounds in series *m*-**P**-10 with one terminal decyloxy ($OC_{10}H_{21}$) tail are summarized in table 2. The compound with the shortest tail (8-**P**-10) shows, on cooling from the isotropic phase, a typical mosaic-like texture characteristic for the B_1 mesophase. All other compounds in this series show spherulitic domains with a fringe pattern on cooling from the isotropic phase. This can be regarded as a typical B_2 pattern [31]. The isotropization temperatures of all six compounds in this series are almost equal (figure 4). The melting points on the other hand decrease with increasing *m*. An explanation for the monotropic behaviour of compound 10-**P**-10 can be found in the symmetric shape of this compound. It is known that symmetric compounds usually have a higher melting point than their non-symmetric analogues [32], as was also found in the *m*-**P**-11 series.

Table 2 and figure 5 show the liquid crystalline properties of the compounds in series *m*-**P**-10a, with the terminal decenyloxy tail. The mesophase behaviour is similar to the compounds of series *m*-**P**-10 although the transition temperatures are lower due to the introduction of the terminal double bond. In contrast to the *m*-**P**-10 series the transition from the B_1 to the B_2 mesophase occurs in series *m*-**P**-10a at $m=10$ to 11, due to the introduction of a double bond. Figure 6 shows the growth of columnar B_1 domains of compound 8-**P**-10a on cooling from the isotropic phase.

The layer spacings *d*, determined from XRD experiments, from the smectic layer structures (B_2 phase) are listed in table 2 and are comparable with the corresponding compounds from the *m*-**P**-11(*a*) series. In both series a linear relationship between *d* and *m* was found.

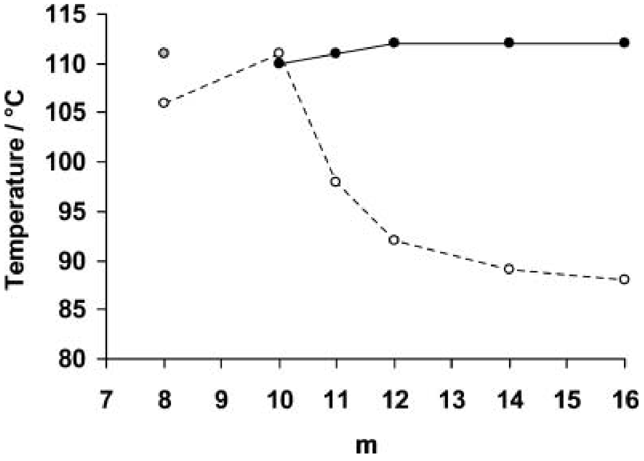


Figure 4. Dependence of the melting points (- -○- -), B_1–I transition (●) and B_2–I transitions (—●—) on *m* for series *m*-**P**-10.

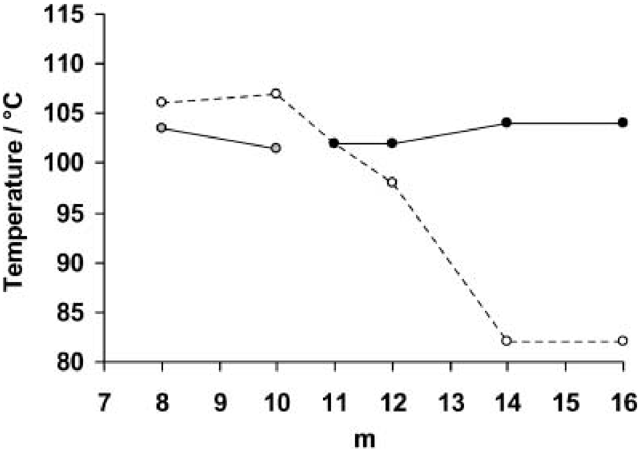


Figure 5. Dependence of the melting points (- -○- -), B_1–I transition (—●—) and B_2–I transitions (—●—) on *m* for series *m*-**P**-10a.

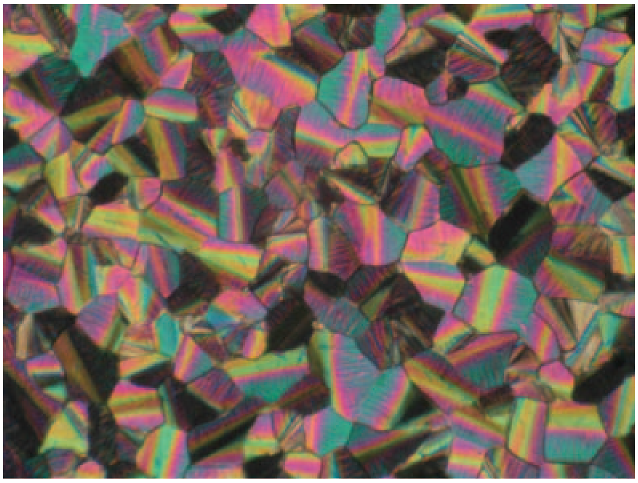


Figure 6. Optical photomicrograph of the growth of B_1 domains of compound 8-**P**-10a on cooling from the isotropic phase.

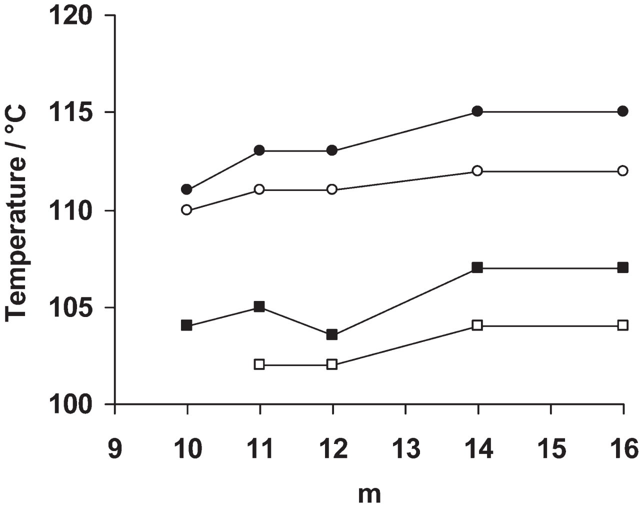


Figure 7. Dependence of the B_2–I transitions of the compounds of series *m*-**P**-11 (—●—), *m*-**P**-11a (—■—), *m*-**P**-10 (—○—) and *m*-**P**-10a (—□—) on *m*.

In all cases a tilt angle of the molecules in the layers of ~45° was calculated.

3.3. *Comparisons between the four series*

Increasing the length of terminal tails suppresses formation of the B_1 phase due to a lack of overlap of the aromatic cores of the antiparallel arranged molecules at the ribbon interfaces [9]. Therefore a B_1 to B_2 transition is often observed in several homologous series upon increasing the terminal tail length. In three of the four series studied the transition from the B_1 to the B_2 phase occurs at $m=8$ to 10. In the *m*-**P**-10a series, however, this transition occurs at $m=10$ to 11. When compared with compound 10-**P**-10 which exhibits the B_2 phase, compound 10-**P**-10a shows the B_1 phase. This must be related to the fact that the latter compound has a terminal vinyl group. Hence we think that the presence of a terminal double bond slightly destabilizes the B_2 phase. It has to be noted however, that according to refs [9, 35] compound 10-**P**-10 shows coexisting B_1 and B_2 phases over a small temperature range.

Figure 7 shows that in all four series the isotropization temperatures increase with *m*. In all cases the isotropization temperature of the long tailed series (*m*-**P**-11 and *m*-**P**-11a) are about 3°C higher than their short-tailed analogues (*m*-**P**-10 and *m*-**P**-10a). On going from the vinyl terminated series (*m*-**P**-10a and *m*-**P**-11a) to the corresponding alkyl terminated series (*m*-**P**-10 and *m*-**P**-11) an increase in isotropization temperature of about 8°C is observed. The melting points of all four series decrease with increasing non-symmetry. The two symmetric compounds have the highest melting points in their series.

3.4. *Compounds with two terminal vinyl groups*

In order to study the influence of double bond-terminated compounds in more detail we have also synthesized compounds 11a-**P**-11a, 10a-**P**-10a and 10a-**P**-11a (table 3). As can be seen from tables 1 and 3 both the isotropization temperatures and the melting points of the compounds in series 11(a)-**P**-11(a) decrease on increasing the number of terminal alkene bonds. The isotropization temperatures, however, decrease faster than the melting point and as a result compound

Table 3. Transition temperatures (°C), transition enthalpies ($\mathrm{kJ\,mol^{-1}}$, in brackets) and layer spacings *d* (Å) of the *ma*-**P**-*na* series.

Compound	Cr	B_1	B_2	I	*d*
10a-**P**-10a[a]	• 102 (69)			•	—
10a-**P**-11a	• 98 (47)	(• 91) (16)		•	—
11a-**P**-11a[a,b]	• 101 (51)		(• 96) (16)	•	34.3

[a] See ref [36]. [b] See ref [37].

11a-**P**-11a shows only a monotropic B_2 mesophase. Remarkably, non-symmetric compound 11-**P**-11a does not show the lowest melting point when compared with symmetric compounds 11-**P**-11 and 11a-**P**-11a. All three compounds 11(a)-**P**-11(a) show antiferroelectric switching behaviour. The introduction of two terminal alkene groups in some cases has been reported to lead to a change in switching behaviour. Whereas 1,3-phenylene bis[4-(4-octyloxyphenyliminomethyl)benzoate] [33] shows an antiferroelectric B_2 phase, the analogue with two terminal alkene bonds, 1,3-phenylene bis{4-[4-(7-octenyloxy)phenyliminomethyl]benzoate} [34] has been reported to show ferroelectric switching.

In tables 2 and 3 the thermotropic properties of compounds 10(a)-**P**-10(a) are given. As in the 11(a)-**P**-11(a) series, a gradual decrease of the melting points is observed on increasing the number of terminal vinyl groups in the 10(a)-**P**-10(a) series. The liquid crystalline behaviour changes completely with increasing number of terminal vinyl groups: 10-**P**-10 monotropic B_2, 10-**P**-10a monotropic B_1, while 10a-**P**-10a showed no mesophase.

In table 3 the thermotropic properties of compound 10a-**P**-11a are shown. Surprisingly, this compound exhibits a monotropic B_1 phase. There are three other compounds with one C_{10} and one C_{11} terminal tail (10-**P**-11, 10a-**P**-11 and 10-**P**-11a). Only compound 10-**P**-11 with no terminal vinyl groups shows an enantiotropic B_2 phase over a reasonable temperature range. Intermediate compounds 10a-**P**-11 and 10-**P**-11a show very similar behaviour: both exhibit the B_2 phase, and the compound with the double bond in the shortest tail (11-**P**-10a) has slightly lower transition temperatures.

4. Conclusions

The introduction of terminal double bonds in banana-shaped compounds lowers both the isotropization temperatures and melting points when compared with the corresponding alkyl-terminated compounds. The B_2 phase is slightly destabilized upon introduction of terminal vinyl groups. The switching behaviour remains antiferroelectric on the introduction of one or two terminal double bonds. Layer spacings and tilt angles of the corresponding compounds with none, one or two terminal vinyl groups are also almost unchanged. The vinyl-terminated compounds described in this paper might be suitable for incorporation as side chains in an oligomeric or polymeric system.

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