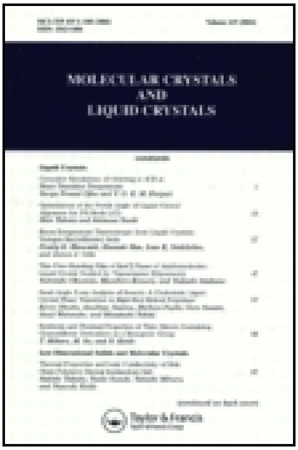

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SYMMETRICAL DIMER LIQUID CRYSTALS WITH TILTED SMECTIC PHASES

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Three series of symmetrical dimer liquid crystals, i.e. bis(dodecyloxybenzoyloxybenzoyloxy)alkanes (BC12) and bis(dodecyloxy- and hexadecyloxybenzoyloxyphenyl) alkanedicarboxylates (QC12 and QC16) with a spacer ranging from two to eight methylene units, have been synthesized and their thermotropic properties were characterized. The isotropization temperatures show a pronounced odd - even effect as a function of the parity of the spacers. Most compounds exhibit a SmC mesophase. The QC12 and QC16 compounds, with an eight methylene spacer, possess an additional low temperature tilted SmI or SmF mesophase. Changing the orientation of the ester group as in the BC12 series results in a dramatic change of the thermotropic behavior.

Keywords: layer spacing; twin liquid crystal; X-ray

INTRODUCTION

Dimeric liquid crystals containing two rigid monomeric units connected via a flexible alkylene spacer, have been investigated intensely in the last decade [1–5]. One of the most important reasons why these compounds gain so much interest is because their properties are quite different from monomeric liquid crystals. Furthermore, their ability to act as model compounds for semi-flexible main-chain liquid crystalline polymers is very important.

We can distinguish two classes of liquid crystalline dimers: non-symmetric [4, 6] and symmetric compounds. The vast majority of dimeric liquid crystals reported in literature may be termed symmetric in that the mesogenic groups are identical. The phase behavior of such compounds is significantly influenced by the structure and length of the spacer as well

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*Corresponding author. E-mail: remko.achten@wur.nl as by the nature and position of the linking groups [7]. The alternations in isotropization temperatures and associated enthalpy changes found for these dimers is attributed to the different number of conformations with parallel (or non-parallel) orientations of the mesogenic units for "odd" and "even" dimers. Though very important, the spacer parity is not the only part of a dimeric liquid crystal that determines the thermotropic properties and liquid crystalline ordering. The mesogenic parts and (alkyl) tails play a very important role as well.

Recently, Choi *et al.* [8] reported that dimeric compounds with a flexible pentyl spacer, α,ω-bis{4-[(4-n-dodecylphenyl)iminomethyl]benzoyloxy}-pentane, gave phases possessing antiferroelectric switching behavior similar to banana-shaped liquid crystals having a 1,3-phenylene core.

We have synthesized three series of dimeric compounds with varying spacer length and studied their liquid crystalline properties. All series contain ester groups as connecting groups between the aromatic rings. In this way the hydrolysis sensitive imine bonds present in the compounds reported by Choi *et al.* were avoided.

EXPERIMENTAL

The series of compounds that we investigated are depicted in Figure 1. The **QC12** and **QC16** series (n = 2–8), which differ in their terminal alkyl chain length (12 vs 16 carbon atoms), were synthesized according to Scheme 1.

Carboxylic acid **I** was transformed into the acid chloride **II** with thionyl chloride and subsequently coupled to an excess of hydroquinone to yield the phenolic compound **III** in 80%. The end products were prepared by direct esterification of the appropriate diacids with the monomeric phenols using N,N′-dicyclohexylcarbodiimide and 4-dimethylaminopyridine as a catalyst.

The **BC12** series (n = 2–8) was synthesized according to Scheme 2. 4-Dodecyloxy-benzoic acid was first reacted with thionyl chloride to its

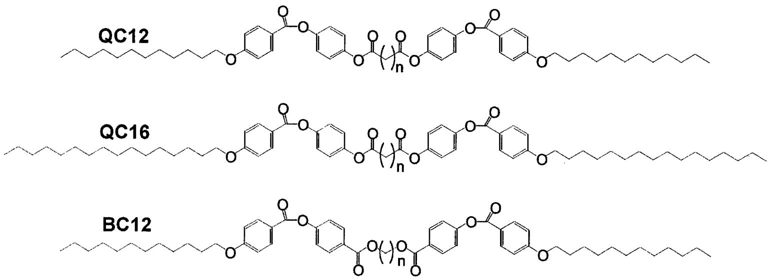
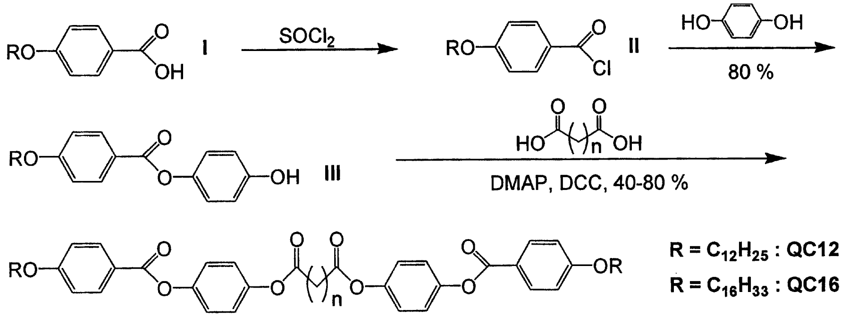


FIGURE 1 Three series of dimer liquid crystals that were studied.

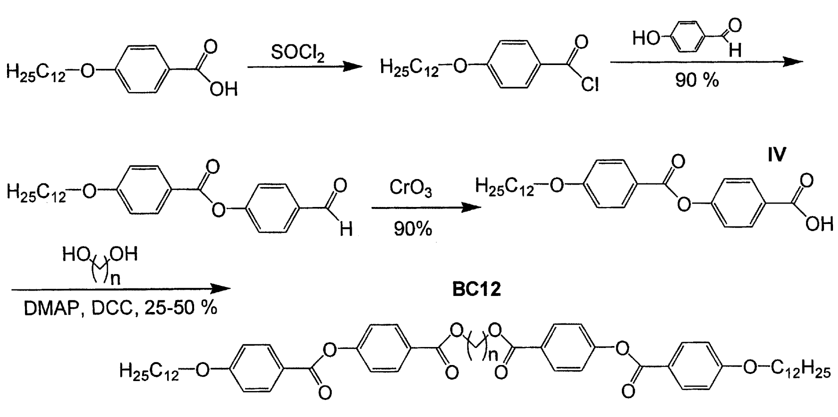


SCHEME 1 Synthesis of series **QC12** and **QC16**.

acid chloride and subsequently coupled to 4-hydroxybenzaldehyde to yield the corresponding aldehyde in 90%. Oxidation of this aldehyde with CrO_3 gave the carboxylic acid **IV** in 90% yield. Finally the dimers **BC12** were prepared by direct esterification of the appropriate diols with the monomeric carboxylic acids using N,N′-dicyclohexylcarbodiimide and 4-dimethylaminopyridine as a catalyst.

RESULTS AND DISCUSSION

The transition temperatures together with the associated transition enthalpies for the series **QC12** and **QC16** are given in Table 1. The thermotropic properties of series **BC12** are given in Table 2. All compounds exhibit liquid crystalline phases, their mesophases were characterized by optical



SCHEME 2 Synthesis of series **BC12**.

TABLE 1 Transition Temperatures (°C) and Transition Enthalpies (kJ mol^{-1}; Between Brackets) for Series **QC12** and **QC16**

Cr		SmX	SmC	N	I
QC12					
n = 2	• 143 [31]		• 195 [13]		•
n = 3	• 141 [49]		• 150 [14]		•
n = 4	• 123 [29]		• 182 [18]		•
n = 5	• 130 [50]		• 135 [6]	• 137 [3]	•
n = 6	• 141 [38]		• 165 [19]		•
n = 7	• 130 [41]		(• 127 [7])	• 132 [3]	•
n = 8	• 131 [28]	• 132 [8]	• 149 [20]		•
QC16					
n = 2	• 137 [32]		• 195 [17]		•
n = 3	• 134 [56]		• 154 [17]		•
n = 4	• 116 [38]		• 180 [18]		•
n = 5	• 124 [58]		• 142 [16]		•
n = 6	• 128 [28]		• 167 [21]		•
n = 7	• 124 [48]		• 136 [18]		•
n = 8	• 121 [35]	• 129 [8]	• 151 [24]		•

polarizing microscopy and differential scanning calorimetry (DSC) as well as by X-ray measurements.

The dependence of the transition temperatures on the length of the spacer of series **QC12** is shown in Figure 2. The clearing temperatures show a marked alternation in which the even members have the higher values. The melting points show no alternating trend. All compounds (n = 2–8) show Schlieren textures indicating a tilted smectic mesophase (SmC). The n = 5 and n = 7 compounds possess an additional nematic mesophase (N) in a narrow temperature interval. This could be caused by the fact that dimers with odd spacers are less ordered in their liquid

TABLE 2 Transition Temperatures (°C) and Transition Enthalpies (kJ mol^{-1}; Between Brackets) for Series **BC12**

BC12	Cr	SmC	SmA	N	I
n = 2	• 131 [55]	• 137 [23]			•
n = 3	• 107 [68]		(• 101 [10])		•
n = 4	• 125 [75]	(• 113 [3])		• 126 [10]	•
n = 5	• 86 [41]		• 98 [10]		•
n = 6	• 104 [44]			• 111 [11]	•
n = 7	• 72 [57]	• 88 [15]			•
n = 8	• 111 [102]			(• 105 [13])	•

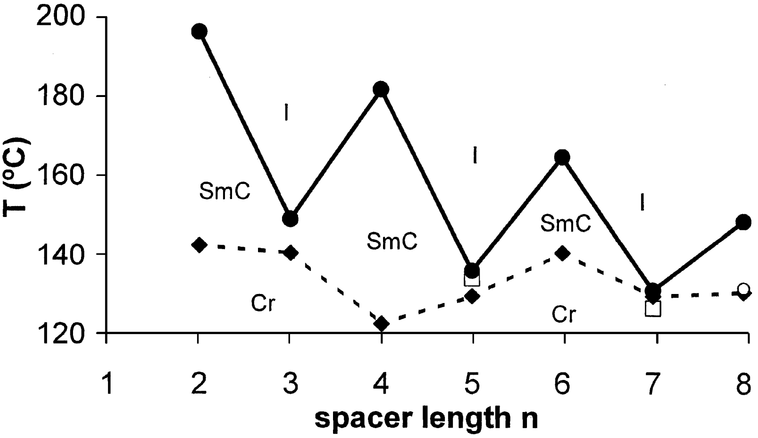


FIGURE 2 Dependence of the melting points (---◆---), SmC-N transitions (□), SmX-SmC transition (o) and isotropization temperatures (—●—) on the number of methylene groups in the spacer of series **QC12**.

crystalline phases than those with even spacers. Most striking is the additional low temperature tilted smectic mesophase (SmX) observed for the n = 8 compound. This transition is indicated by a partial disappearance of the Schlieren texture, and appearance of a focal conic-like texture (Fig. 3).

From the Bragg reflections in the small angle region, the layer spacings d from the smectic layers in series **QC12** were determined (Fig. 4). It was found that the layer spacings for the smectic phases do not change markedly with temperature. Figure 4 shows that the n = 8 compound exhibits two smectic modifications. The layer spacing increases discontinuously at the smectic-smectic transition.

From the broad wide angle diffraction band a liquid-like order in the SmC mesophase is confirmed. The low temperature smectic mesophase for n = 8 shows one sharp peak in the wide angle region at 4.5 Å. This corresponds to the side-to-side separation of the molecules and points to a tilted hexatic phase (SmI or SmF).

The thermotropic properties of series **QC16** are also given in Table 1. Their properties are very similar to those of the **QC12** series, except that the nematic phases are absent in this series. As in the **QC12** series the compound with n = 8 shows two smectic phases.

The thermotropic behavior of series **BC12** in which the ester bond between the mesogenic units and the spacer is reversed is given in Table 2. The small change in chemical structure (**QC12** vs **BC12**) changes the liquid crystalline properties of these compounds dramatically. The liquid

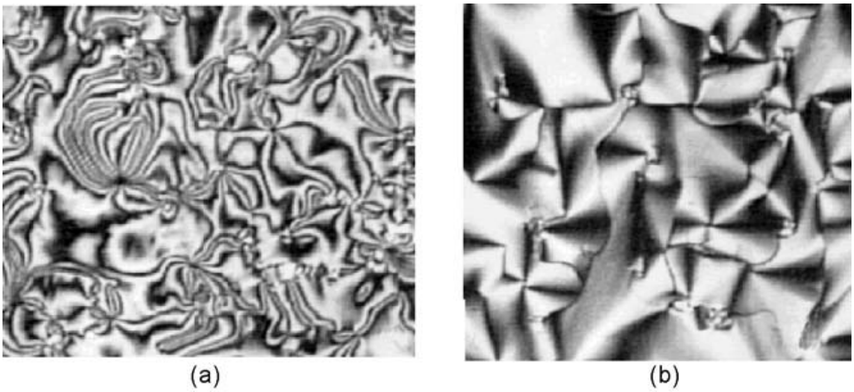


FIGURE 3 Optical texture change from a) SmC (145°C) to b) SmX (130°C) for **QC12** n = 8.

crystalline range becomes significantly smaller and three different mesophases are present in this series. The n = 6 and 8 compounds have only a nematic phase, the n = 3 and 5 compounds are only SmA and the n = 2 and 7 compounds only shows a tilted smectic phase (SmC). The n = 4 compound has a SmC-N transition. Apparently, in this series the tilted smectic phases quickly become unfavorable for the even members and for the higher members only nematic phases are observed, while the ordering of the odd members increases from SmA for n = 3 and 5 to a tilted smectic for n = 7.

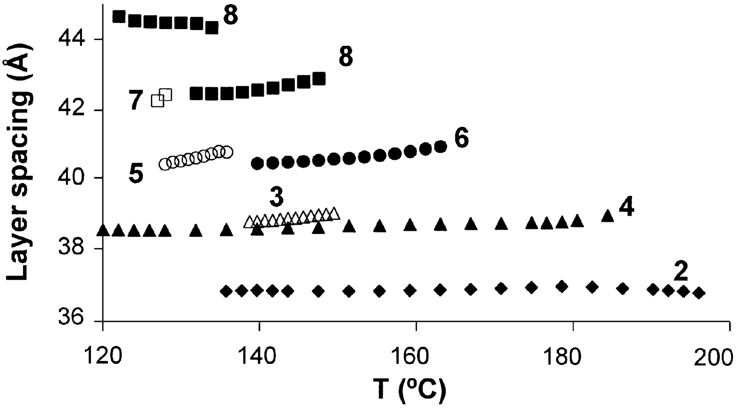


FIGURE 4 Dependence of the layer spacings on the temperature of series **QC12** (n = 2–8).

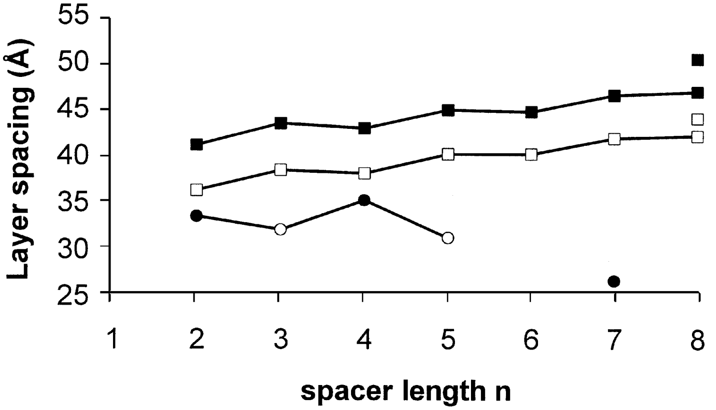


FIGURE 5 Dependence of the average layer spacings of the **QC12** series (—□—), the **QC16** series (—■—) and the **BC12** series (SmA (—○—) and SmC (—●—)) on the number of methylene groups in the spacer.

The layer spacings for the three series of compounds are depicted in Figure 5. The layer spacings for the **QC12** and **QC16** series increase with increasing spacer length as one would expect. The layer thickness of the **QC16** compounds is on average 4.8 Å larger than of the corresponding **QC12** compounds. The increase in layer spacings with spacer length is not linear; this is probably caused by different conformations or tilt angles of the "odd" molecules in comparison with the "even" molecules. At the transition from the SmC to the higher ordered tilted mesophase for the n = 8 compounds the layer spacings increases ~2 Å (**QC12**) and ~3 Å (**QC16**). These changes in layer spacings are probably caused by the formation of the hexatic mesophase accompanied by a decrease in tilt angle of the molecules.

The layer spacings for the **BC12** series show an unexpected behavior since they decrease with increasing spacer length. For the SmC compounds (n = 2, 4 and 7) there is a transition to an intercalated layer structure for the n = 7 compound since the estimated all-*trans* molecular length of this compound is about twice the layer thickness. The larger layer spacing for the n = 3 SmA compounds in comparison with the n = 5 SmA compound is still unclear. The absence of a smectic phase for n = 6 could indicate a spacer dependent change in smectic modification upon going from short to long spacers.

Electrooptical studies will be performed to determine whether some of these compound are banana-shaped and exhibit (anti)ferroelectric switching behavior.

CONCLUSIONS

All the compounds of the three series of dimers exhibit liquid crystalline phases. The compounds of the **QC12** and **QC16** series show a tilted smectic mesophase (SmC) and a strong odd-even effect in the isotropization temperatures. The increase in terminal alkyl tail suppresses the nematic mesophase. With decreasing temperature both n = 8 compounds show an additional tilted hexatic mesophase, probably smectic I or F. This low temperature mesophase has an increased layer spacing probably caused by a change in tilt angle.

A small change in chemical structure (**QC12** vs **BC12**) results in a dramatic change in liquid crystalline properties of the **BC12** series. Besides tilted smectic amd nematic phases these compounds also form SmA phases. The layer spacings of the smectic phases of this **BC12** series show an unexpected trend since there is a slight decrease in layer spacings for the compounds with the longest spacers. This could be related to a change from monolayer smectic structure for small n to an interdigitated smectic structure for longer n. The odd and even members of this series seem to show a different trend with increasing spacer length.

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