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## Liquid Crystals

Publication details, including instructions for authors and subscription information:

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Antonius T. M. Marcelis<sup>a</sup>; Marcel Giesbers<sup>a</sup>; Arie Koudijs<sup>a</sup>

<sup>a</sup> Laboratory of Organic Chemistry, Wageningen University and Research Center, 6703 HB Wageningen, The Netherlands

**To cite this Article** Marcelis, Antonius T. M. , Giesbers, Marcel and Koudijs, Arie(2007) 'Spacer length dependence of TGBC\* and SmA phases in cholesteryl and dihydrocholesteryl-containing trimer liquid crystals', *Liquid Crystals*, 34: 7, 811 – 817

**To link to this Article:** DOI: 10.1080/02678290701478798

**URL:** <http://dx.doi.org/10.1080/02678290701478798>

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# Spacer length dependence of TGBC\* and SmA phases in cholesteryl and dihydrocholesteryl-containing trimer liquid crystals

ANTONIUS T.M. MARCELIS\*, MARCEL GIESBERS and ARIE KOUDIJS

Laboratory of Organic Chemistry, Wageningen University and Research Center, Dreijenplein 8, 6703 HB Wageningen, The Netherlands

(Received 19 February 2007; accepted in revised form 7 May 2007)

Two series of trimer liquid crystals were investigated that contain a biphenyl central group and two cholesteryl or dihydrocholesteryl terminal mesogenic groups. Only compounds with even spacers were investigated. The dihydrocholesteryl-containing trimers show a triply intercalated smectic A (SmA) phase when the spacer lengths are greater than 8, whereas the cholesteryl-containing trimers exhibit this triply intercalated SmA phase when the spacer lengths are more than 6. With shorter spacers, a twist grain boundary C\* (TGBC\*) phase was found. This is revealed by the formation of a typical dotted square grid pattern upon cooling from the chiral nematic (N\*) phase in the planar texture. The dots are spaced by a distance of about 1.5–1.8  $\mu\text{m}$ . Upon cooling from the N\* phase in the focal conic texture a striped pattern is observed with the same spacing. X-ray diffraction revealed a repeat distance for the TGBC\* phase that corresponds with a monolayer ordering. The results show that the weaker interaction between the dihydrocholesteryl groups compared with cholesteryl groups or longer spacers destabilize the monolayer TGBC\* phase.

## 1. Introduction

Dimer liquid crystals show interesting properties, such as an enhanced odd–even effect of the physical properties as a function of spacer parity [1–3]. This strong odd–even effect is, for example, found for the isotropization temperatures and the corresponding isotropization enthalpies. Furthermore, the ordering of these molecules in their smectic phases shows a wide variety of possibilities. Depending on the ratio between spacer length and terminal tail length and on the nature of the mesogenic groups, intercalated, interdigitated and monolayer organizations of the smectic phases have been observed. The type of organization also depends on whether the two mesogenic units are identical or different. These different smectic organizations have been well investigated for dimers with two identical or two different aromatic mesogenic units [1–9] and also for dimers in which one of the mesogenic groups is an aromatic mesogenic group and the other a significantly different (dihydro)cholesteryl group. For these (dihydro)cholesteryl-containing compounds, monolayer, interdigitated and intercalated smectic phases are also observed, in addition to a chiral nematic phase [10–23].

Trimer liquid crystals with two flexible spacers between the mesogenic units have also been investigated, although less thoroughly. Trimers that consist of three aromatic mesogenic groups have been investigated and also several compounds that contain one or two steroidal mesogenic groups [24–33]. For the latter compounds, nematic phases are commonly observed but trimers that form smectic phases are also known [30–33]. During our research on dihydrocholesteryl-containing dimers and trimers, we observed smectic phases in some trimers consisting of a central biphenyl mesogenic unit, coupled to two dihydrocholesteryl groups via alkanate spacers [30]. In this specific series of compounds smectic phases were only observed when both spacers were even. However, for other types of trimers smectic phases were also observed for compounds with odd spacers [26, 32]. The most likely possibilities for ordering of the smectic phases of these trimeric compounds are a monolayer ordering in which the smectic layer spacing corresponds approximately to the length of the molecule or intercalated structures in which the smectic layer thickness corresponds to one-third of the total length of the molecules. Both types of structural ordering have been observed. A monolayer ordering for trimer liquid crystals was observed for bischolesteryl compounds with a 1,4-bis(phenylethenyl)benzene group as fluorescent central mesogenic group [33] and some trimeric compounds

\*Corresponding author. Email: ton.marcelis@wur.nl

containing three biphenyl groups [28]. Triply intercalated compounds were observed for some azobenzene containing compounds [26].

An interesting aspect of cholesteryl- or dihydrocholesteryl-containing dimer and trimer liquid crystals is that the chirality can give rise to frustrated orderings, such as blue phases and twist grain boundary phases [34]. Recently, a so-called undulated twist grain boundary C\* (or UTGBC\*) phase was found for some cholesteryl containing trimer liquid crystals [31, 32]. This phase has also been described for several other chiral compounds, among others for cholesteryl-containing dimers [14, 22, 23, 35]. There is some debate in the literature about the exact structure of this phase and whether they are all the same. It is clear that they are the result of extreme frustration. These phases are also known under other names, such as S-TGBC, TGBC\* and giant block TGBC\* [36–40]. A feature often found for these phases is the appearance of an optical square grid pattern in some orientations of the liquid crystalline phase under a polarizing microscope. In some cases this phase exists for only a few degrees Celsius, but in other cases this phase is observed in a wide temperature range.

In this study a series of previously investigated dihydrocholesteryl-containing trimers is reinvestigated together with several other members of this series and similar series of trimer liquid crystals that contain two terminal cholesteryl groups or one cholesteryl and one dihydrocholesteryl group [30].

## 2. Experimental

### 2.1. Synthesis

**2.1.1. General procedure for the preparation of the trimer liquid crystals I-n,m, II-n,m and III-n,m.** A mixture of 1.1 mmol of cholesteryl or dihydrocholesteryl  $\omega$ -bromoalkanoate [15], 1 mmol of cholesteryl or dihydrocholesteryl  $\omega$ -(4'-hydroxybiphenyloxy)alkanoate [30] and 1 g of anhydrous  $K_2CO_3$  was refluxed for 1–2 days in 20 ml of butanone. The reaction mixture was then concentrated and 20 ml of dichloromethane was added. After filtration of the salts and evaporation of the solvent, the residue was purified by column chromatography on silica gel with dichloromethane as eluent. A final recrystallization from hexane or hexane/ethyl acetate afforded the pure compounds.  $^1H$  NMR, elemental analyses and thin layer chromatography confirmed the structure and purity of the products.

### 2.2. Measurements

Melting points, thermal phase transition temperatures and optical inspection of the liquid crystalline phases

were investigated using samples between ordinary glass slides using an Olympus BH-2 polarizing optical microscope (POM) equipped with a Mettler FP82HT hot stage, controlled by a Mettler FP80HT central processor. Differential scanning calorimetry (DSC) thermograms were obtained on a Perkin Elmer DSC-7 system using 1–3 mg samples in 30  $\mu$ L sample pans and a scan rate of 5 or 10  $^{\circ}C\ min^{-1}$ . Transition enthalpies ( $\Delta H$ ) were calculated in  $\text{kJ mol}^{-1}$ . Temperature-dependent X-ray curves were measured on a Philips (Panalytical) X'pert Pro 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 the liquid crystalline phase on a thin glass slide (about 15  $\mu$ m thick) which was placed on a temperature-regulated flat copper sample stage.

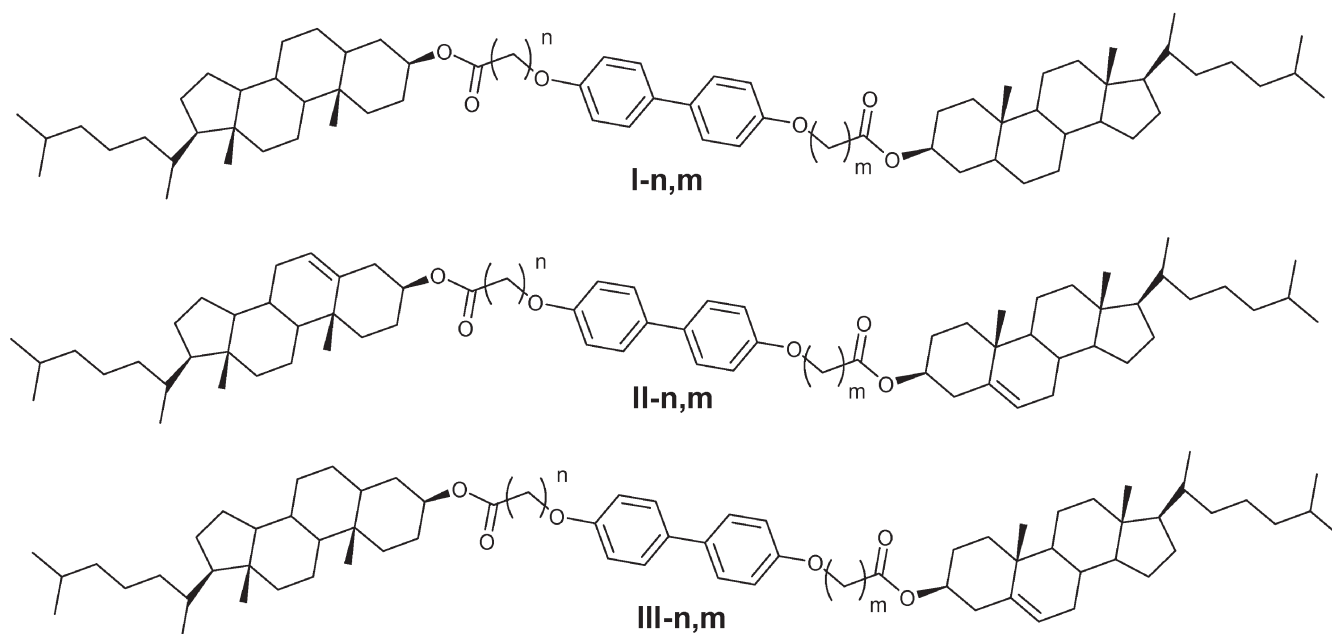
## 3. Results and discussion

The structures of the compounds that were studied are given in scheme 1.

The compounds were synthesized according to scheme 2. The synthetic procedure has been described previously for the corresponding dihydrocholesteryl compounds **I-n,m** [30].

In these series of compounds all spacers are even, since the number of flexible units between the mesogenic groups are equal to  $nCH_2 + C=O (+2 -O-)$ . It was previously shown that for the investigated compounds with one or two odd spacers, only chiral nematic (N\*) phases were found [30]. All compounds **I-n,m**, **II-n,m** and **III-n,m** showed a N\* phase. Furthermore, they all showed a transition to another phase upon cooling from the N\* phase. It soon became apparent that this was not always a smectic A (SmA) phase. Close inspection of the polarized optical textures showed that in many cases a dotted square grid pattern was formed upon cooling the N\* phase in the planar or Grandjean texture. Such textures have been observed before and are very typical of the twist grain boundary C\* (TGBC\*) phase observed, amongst others, for some trimer liquid crystals that contain cholesteryl groups [31, 32]. When longer spacers are used there is a transition from N\* to a regular SmA phase. The phase transition temperatures of the dihydrocholesteryl compounds **I-n,m** are given in table 1, together with the  $d$  spacings obtained by X-ray diffraction (XRD), the calculated length  $L$  of the molecule and the  $d/L$  ratio.

The N\*–isotropic (I) transition temperatures gradually decrease with increasing total spacer length,  $n+m$ . (figure 1). The enthalpy change at the N\*–I transitions, which for dimers and trimers shows a strong odd–even effect with spacer parity are all in the same range,



Scheme 1. Structures of the investigated compounds.

because in this case all spacers are even. The transition from  $N^*$  to SmA or TGBC\* phases has a very low enthalpy, and in several cases this transition was not observed by DSC. This has also often been observed for transitions to the TGBC\* phase [23, 32, 35]. POM observations of this transition were, however, very clear. The compounds with the longer spacers,  $n+m \geq 10$ , show textures that point to a SmA phase, i.e. well-developed fans (figure 2 a). XRD measurements of these phases indicate spacings of about one-third of the length of the molecules in their most stretched

conformations (see figure 3), which point to triply intercalated smectic phases, as have been observed previously for trimer liquid crystals [26]. Another observation that is worth mentioning is that the  $N^*$ -SmA transition is sharp, as observed by POM, i.e. it is not accompanied by a TGBC phase. Similar behaviour was observed before for transitions of chiral dimers from the  $N^*$  phase to an intercalated SmA phase [9, 17].

The compounds with short spacers, **I-3,3** and **I-3,5**, show textures that indicate a TGBC\* phase. Upon cooling the planar oriented  $N^*$  phase in which the

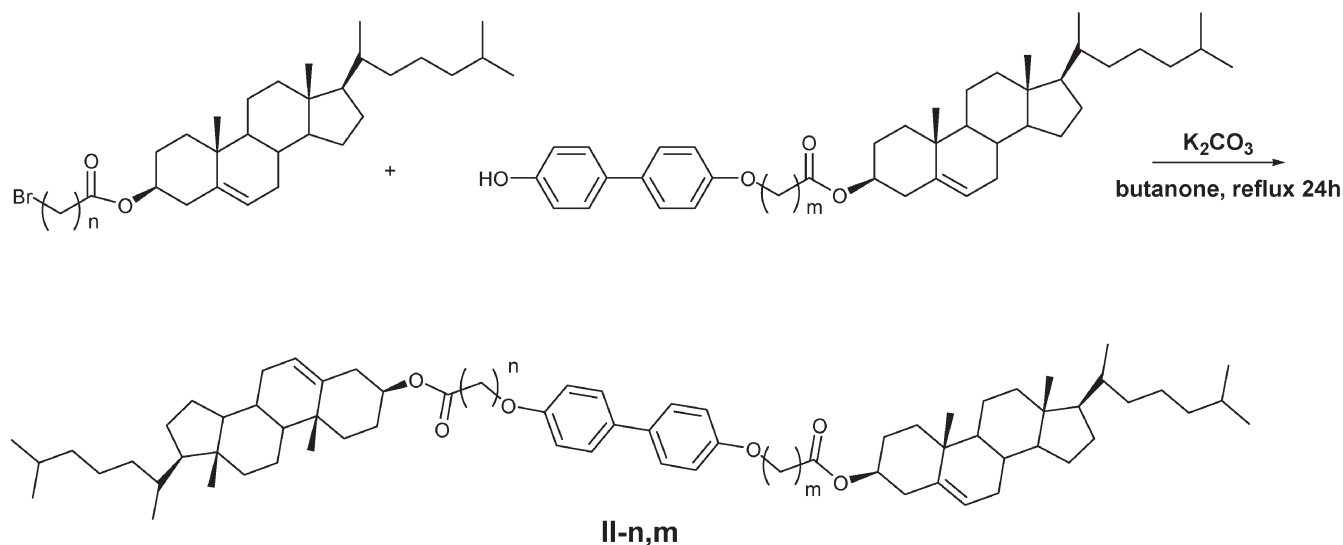
Scheme 2. Synthetic scheme for compounds **II-n,m**.

Table 1. Melting points, phase transition temperatures ( $^{\circ}\text{C}$ ) and enthalpies ( $\text{kJ mol}^{-1}$ , in brackets),  $d$  spacings of the SmA (or TGBC\*) phase, estimated length  $L$  of the molecules and  $d/L$  ratios of compounds **I-n,m**, **II-n,m** and **III-n,m**.

Compound	M.p.	TGBC*-N*	SmA-N*	N*-I	$d/\text{\AA}$	$L/\text{\AA}$	$d/L$
<b>I-3,3</b>	200 (35)	213 (<0.1)		255 (9.0)	57.9	58	1.00
<b>I-3,5</b>	182 (32)	190 (<0.1)		240 (8.7)	18.7	62	0.30
<b>I-5,5</b>	178 (37)		178 (0.2)	227 (10.0)	18.7	62	0.30
<b>I-5,7</b>	155 (33)		179 (0.2)	212 (9.9)	20.1	68	0.30
<b>I-7,7</b>	152 (60)		178 (0.4)	199 (10.2)	20.1	68	0.30
<b>II-3,3</b>	187 (41)	235 (<0.1)		269 (10.3)	58.3	58	1.00
<b>II-3,5</b>	165 (25)	211 (0.1)		252 (10.1)	59.4	60	0.99
<b>II-5,5</b>	160 (24) <sup>a</sup>	183 (0.1)		239 (10.0)	61.3	62	0.99
<b>II-5,7</b>	151 (33)	160 (0.2)		223 (9.2)	63.0	65	0.97
<b>II-7,7</b>	151 (59)	[140 (0.3)] <sup>b</sup>	184 (0.3)	213 (9.6)	20.0	68	0.29
<b>III-3,3</b>	189 (44)	227 (<0.1)		262 (10.1)	59.2	58	1.04
<b>III-3,5</b>	171 (27)	200 (<0.1)		245 (9.7)	59.9	60	1.00
<b>III-5,5</b>	166 (30)	178 (<0.1)		233 (9.8)	59.8	62	0.96

<sup>a</sup>An additional m.p. was found at  $151^{\circ}\text{C}$ . <sup>b</sup>Upon cooling the SmA phase to about  $142^{\circ}\text{C}$ , a re-entrant N\* phase forms, which upon further cooling for a few degrees transforms into a TGBC\* phase.

helical axis points parallel to the light direction, a grid of dots in a square arrangement is observed (figure 2 b). At the same time, the colour from the selective reflection wavelength is replaced by a grey background. Upon cooling the N\* phase in the focal conic texture, a striped pattern is formed at the transition to the TGBC\* phase (figure 2 c). Both the spacing between the dots and the distance between the lines are of the order of  $1.5\text{--}1.8\ \mu\text{m}$ . A similar period of the grid ( $1.75 \pm 0.25\ \mu\text{m}$ ) was observed by Ribeiro *et al.* for a phase they called S-TGBC [39]. The fact that these grid patterns can be seen has been related to a commensurate TGBC\* phase [40].

XRD studies of these phases reveal a rather weak peak that corresponds to the length of the molecules. This indicates that the tilt angle expected for a smectic C (SmC) type of phase is only very small. Tilt angles reported in the literature for TGBC\* phases, although for quite different compounds, are around  $30\text{--}35^{\circ}$  [35, 39].

For the corresponding cholesteryl compounds, **II-n,m**, similar behaviour and phases are found. The phase transition and XRD data are also given in table 1. However, the polarized optical textures for this series indicate that only TGBC\* phases are found below the

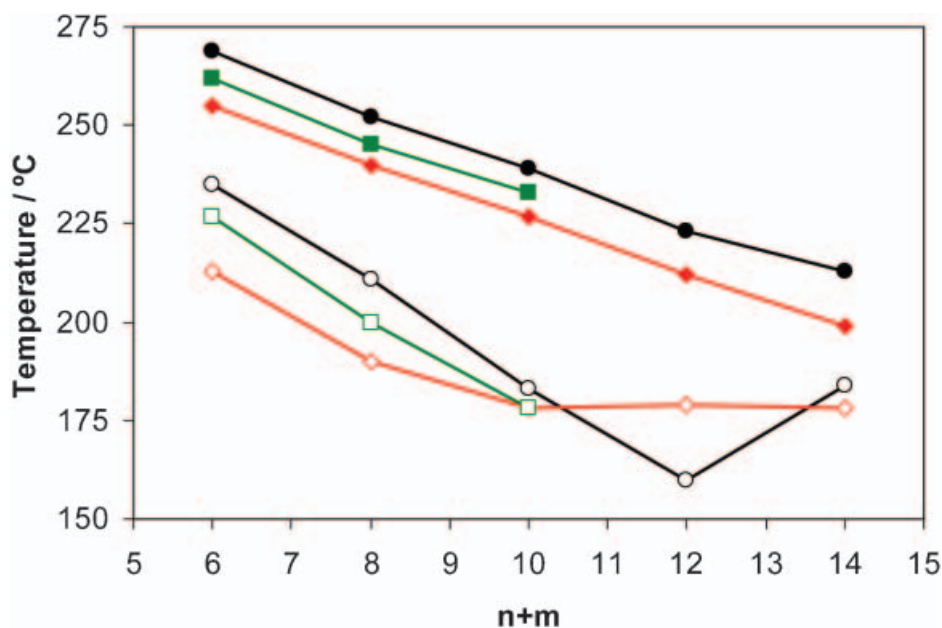


Figure 1. Dependence of the SmA-N\* and TGBC\*-N\* (open symbols) and N\*-I (filled symbols) transition temperatures of compounds **I-n,m** (diamonds), **II-n,m** (circles) and **III-n,m** (squares) on the total number of methylene groups ( $n+m$ ) in the spacers.



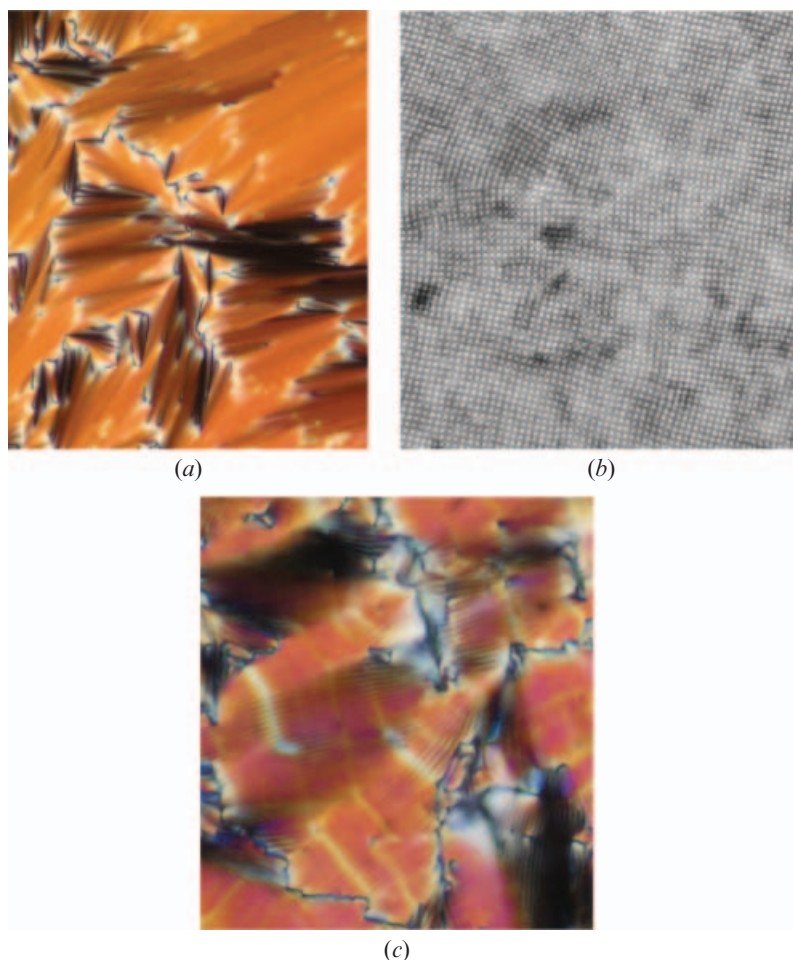


Figure 2. Textures for compound **I-7,7** in the SmA phase (a) and textures observed upon cooling of compound **I-3,3** from the N\* phase in a planar texture (b) or from a focal conic texture (c) into the TGBC\* phase.

N\* phases, except for the compound with the longest spacers, **II-7,7**, which displays a texture indicative for a SmA phase. This is confirmed by XRD of this

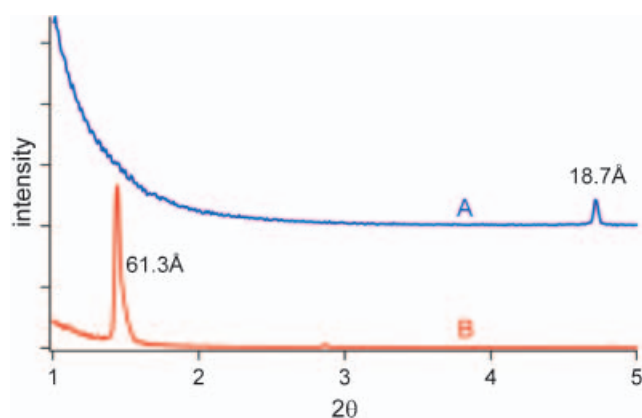


Figure 3. Small-angle XRD graphs of compound **I-5,5** (A) and **II-5,5** (B) both at 175°C.

compound which shows a triply intercalated smectic phase, like several compounds in series **I-n,m** with longer spacers. The difference between the two series is clear from the XRD profiles of compounds **I-5,5** and **II-5,5** which clearly indicate a triply intercalated SmA phase for **I-5,5** and a monolayer structure for **II-5,5** (figure 3). For compound **II-7,7**, cooling of the SmA phase to 142°C, results in formation of a re-entrant N\* phase, which is transformed a few degrees lower at about 140°C into a TGBC\* phase. Since this is a monotropic transition, crystallization prevented determination of the layer spacing of this phase by XRD. It was however clear that the XRD peak of the *d* spacing of the SmA phase disappeared at the transition from the SmA to the re-entrant N\* phase.

Finally, we investigated three compounds with one cholesteryl group and one dihydrocholesteryl group, **III-n,m** (table 1). In compounds **III-3,5**, the cholesteryl group is attached to the shortest spacer. All these three compounds show the TGBC\* phase below the N\*

phase, as was clear from both optical textures and XRD measurements (see table 1).

When all the N\*–I transition temperatures are plotted versus the total spacer length,  $n+m$ , it is clear that within each series the transition temperatures gradually decrease with spacer length (figure 1). The cholesteryl compounds have the highest transition temperatures, the dihydrocholesteryl the lowest, and those with one cholesteryl and one dihydrocholesteryl group have the isotropization temperatures between these series. This is an indication that the cholesteryl compounds have better liquid crystalline properties, as is already known. When the transitions to the lower temperature phase are plotted, there is a break in the curves between  $n+m=12$  and 14 for the cholesteryl compounds, **II-n,m**, and at about  $n+m=10$  for the dihydrocholesteryl compounds, **I-n,m**. This break corresponds with the change from TGBC\* to SmA phases. The TGBC\*–N\* transition temperatures decrease regularly with increasing  $n+m$ . For these examples it is also seen that the chiral nematic range increases with increasing  $n+m$ . This indicates that the TGBC\* phase is destabilized with increasing spacer length.

A reason for the different behaviour as a function of steroidal mesogenic group and of spacer length may be that in principle a monolayer ordering is preferred, because this would give the best overlap between the mesogenic steroidal groups. Such an ordering is, however, destabilized by the relatively small cross-sectional areas of the alkyl spacers and the biphenyl groups compared with the cross-sectional areas of the steroidal groups. In such a situation it is expected that the nematic range increases upon increasing the length of the spacers, because the longer spacer lengths destabilize the smectic phase. This is indeed observed. Something similar was also observed for interdigitated SmA phases of dimers containing cholesteryl groups [15, 18]. When the mesogenic interaction between the steroidal groups is weaker, as in the dihydrocholesteryl trimers, or when the spacer length becomes too long, as in compound **II-7,7**, a monolayer ordering cannot be maintained and as an alternative a triply intercalated SmA phase is formed.

Apparently, the triply intercalated SmA phase for compound **II-7,7** is not very stable since supercooling to about 140°C results in re-entrant behaviour and the SmA phase reverts to the N\* phase, which subsequently transforms into a TGBC\* phase. On the other hand, a normal SmA monolayer structure is also not stable and the layer structure is distorted to form instead a TGBC\* phase.

The  $d$  spacings for the compounds in the SmA phase increase regularly with increasing total spacer length. It

is about one-third of the calculated length of the molecules in their fully stretched conformation. The organization in the SmA phase of these compounds can thus be described as triply intercalated, with layers consisting of randomly mixed biphenyl groups and (dihydro) cholesteryl groups in a 1:2 ratio, separated by layers consisting of alkyl spacers and tails.

#### 4. Conclusions

Trimer liquid crystals with two cholesteryl or dihydrocholesteryl mesogenic groups and a biphenyl central group connected by even spacers show, in addition to a N\* phase, a triply intercalated SmA or a monolayer TGBC\* phase. Which phase is formed depends on the spacer length and on the nature of the steroidal group. Short spacers and a good mesogenic group, e.g. a cholesteryl group, favour monolayer ordering, which because of frustration becomes a TGB\* phase. Destabilization of this structure by longer spacers or the presence of the weaker mesogenic dihydrocholesteryl group results in a triply intercalated SmA phase.

#### Acknowledgements

The syntheses of several new compounds were performed by undergraduate students Jurriaan Bakker, Martine Bokma, Linda Klauss and Niels ten Brummelhuis.

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