

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Dimer liquid crystals with bent mesogenic units

Antonius T. M. Marcelis^a; Arie Koudijs^a; Ernst J. R. Sudhölter^a

^aLaboratory of Organic Chemistry, Wageningen University, Dreijenplein 8, 6703 HB Wageningen, The Netherlands,

Online publication date: 06 August 2010

To cite this Article Marcelis, Antonius T. M. , Koudijs, Arie and Sudhölter, Ernst J. R.(2010) 'Dimer liquid crystals with bent mesogenic units', *Liquid Crystals*, 27: 11, 1515 – 1523

To link to this Article: DOI: 10.1080/026782900750018681

URL: <http://dx.doi.org/10.1080/026782900750018681>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Dimer liquid crystals with bent mesogenic units

ANTONIUS T. M. MARCELIS*, ARIE KOUDIJS
and ERNST J. R. SUDHÖLTER

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

(Received 22 March 2000; accepted 19 May 2000)

Three series of dimer liquid crystals containing an aromatic and a cholesteryl mesogenic unit were synthesized and investigated. The compounds within the series differ in the length of the spacer connecting the mesogenic groups. Two of the three series contain an aromatic mesogenic group that is connected to the spacer at a *meta*-position instead of the *para*-position. Due to the presence of this bent mesogenic group, the odd–even effect in the transitional properties that is normally observed for dimer liquid crystals is reversed as compared with that of the third series, which contains a *para*-substituted aromatic mesogenic group. The reversed odd–even effect is found for the isotropization temperatures, the associated enthalpy changes and also for the optical properties.

1. Introduction

Dimer or twin liquid crystals are a class of liquid crystals in which two rigid mesogenic units are joined by a flexible spacer. One of the most interesting features of these dimers is that the phase transitional properties exhibit a dramatic dependence on the length and especially the parity of the connecting spacer [1–3]. A similar dependence was also found for main chain polymer liquid crystals with flexible spacers between the mesogenic units, and therefore it has been suggested that dimer and also trimer and oligomer liquid crystals can serve as useful model compounds for main chain liquid crystal polymers. The pronounced alternations in isotropization temperatures and associated entropy changes found for these dimers is attributed to the different number of conformers with parallel orientations of the mesogenic units for odd and even dimers. A theoretical model has recently been developed to explain these differences. For dimers connected with an even spacer, more parallel orientations of the mesogenic groups are possible than for dimers connected by an odd spacer.

In recent studies on chiral dimers and trimers it was found that the selective reflection wavelength of the chiral nematic phase also exhibits a strong dependence on the number of flexible units between the mesogenic groups [4–7]. The better ordered members of the series exhibit higher selective reflection wavelengths. When such compounds are present as a guest in a (chiral) nematic host, the same trend in helical twisting power was observed [8]. This technique was found useful for

investigating the optical properties when the selective reflection wavelength of the pure compounds could not be measured for all members of a series. This is the case when (i) the series contains members that decompose at high temperatures, (ii) when some members have no liquid crystalline phases or only monotropic transitions, (iii) not all members exhibit a chiral nematic phase or (iv) the selective reflection wavelength lies outside the range of the apparatus.

During our recent studies on trimer liquid crystals consisting of a central estradiol moiety connected to two terminal cyanobiphenyl groups via flexible spacers, indications were found for a reversed odd–even effect for the spacer attached to the hydroxyl group at the 17-position of estradiol [9, 10]. This is attributed to the fact that the bond connecting the mesogenic unit with the spacer makes a considerable angle with the long axis of the central mesogenic unit, whereas in other dimer liquid crystals this bond is parallel with the long axis of the mesogenic unit. To investigate the influence of this angle on the liquid crystalline properties of dimers in more detail, we decided to study some liquid crystals with a *meta*-bond instead of a *para*-bond connecting the mesogenic unit with the spacer. The influence of the group that connects *para*-substituted mesogenic units with the spacer has been studied before [1, 3, 11, 12]. It was found that when the angle between mesogenic unit, connecting group, and alkyl spacer increases as in the series methylene, oxygen and carbonate, the odd–even effect becomes less pronounced. The compounds that are the subject of the present investigation can better be compared with so-called laterally substituted liquid crystals [13]. In an example of a series that was not

* Author for correspondence
e-mail: ton.marcelis@phys.oc.wau.nl

described as a dimer liquid crystal, but as a liquid crystal laterally substituted with a flexible chain ending in a phenyl group, it was found that the higher mesophase stability was observed for the odd membered spacers [14]. For some T-shaped liquid crystals [15] and for laterally connected H-shaped liquid crystals, clear normal odd–even effects have been observed [16, 17]. Studying the properties of non-linear mesogenic units may also be relevant for the so-called banana liquid crystals, which exhibit new and fascinating liquid crystalline phases due to their bent shapes [18–20]. Some dimer liquid crystals have also been reported to exhibit these ‘banana’ phases [21, 22].

For the present study we chose mesogenic units with only weak dipoles to exclude strong dipolar interactions. Furthermore, we used dimers with a cholesteryl group as one of the mesogenic units in order to investigate the influence of the attachment on the ordering by studying the chiroptical properties.

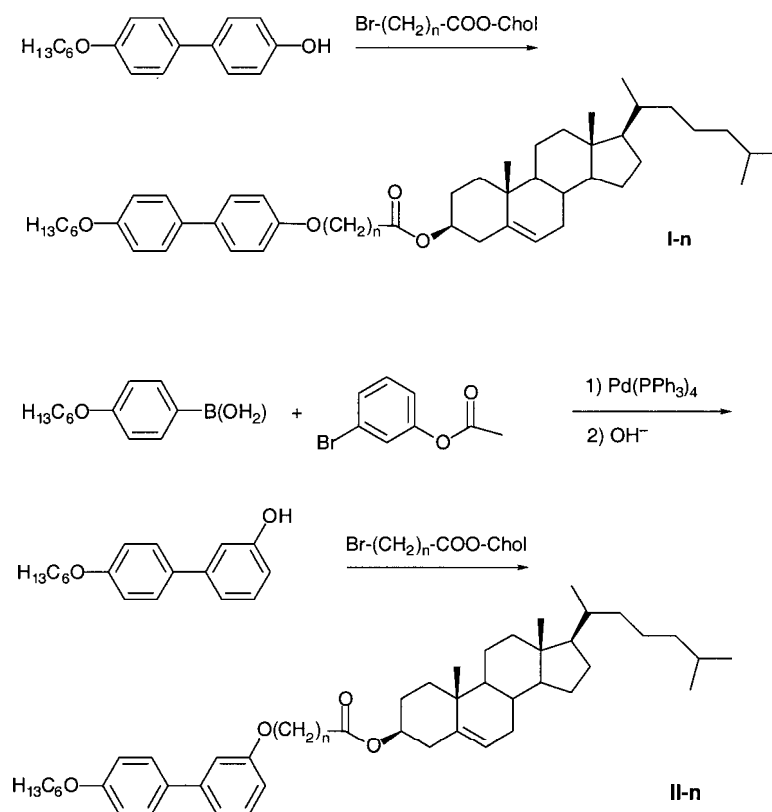
2. Experimental part

2.1. Synthesis

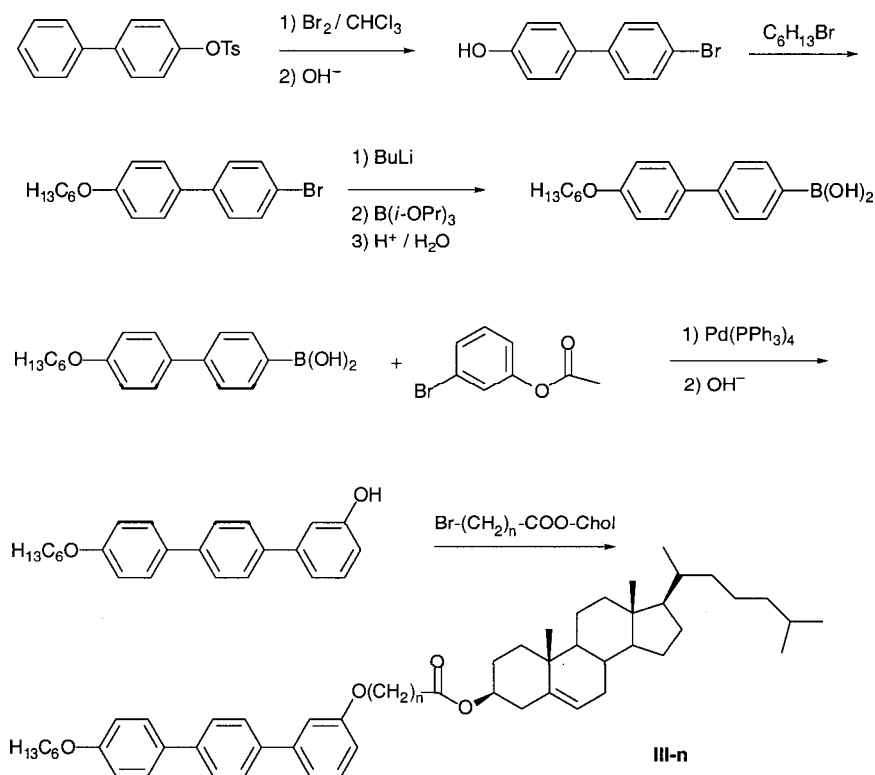
The synthesis of the liquid crystal materials is depicted in schemes 1 and 2. Compounds **I-n** were prepared from 4-hexyloxy-4'-hydroxybiphenyl [23]. For compounds **II-n**, 4-hexyloxy-3'-hydroxybiphenyl was prepared first by a Suzuki cross-coupling of 4-hexyloxyphenylboronic

acid [24] with 3-bromophenyl acetate. For the synthesis of 4-bromo-4'-hydroxybiphenyl used for the preparation of **III-n** several procedures have been described. A simple method based on bromination of 4-biphenyl benzenesulphonate in acetic acid and reported to give high yields [25] proved to be irreproducible by us and several other investigators [26–28]. Percec *et al.* described two other methods, one based on bromination of 4-nitrobiphenyl, followed by conversion of the nitro group into a OH group in two steps [26] and another method based on bromination of the acetate of 4-phenylphenol [27]. Recently, 4-bromobiphenyl derivatives have been prepared by coupling phenylboronic acids with 1-bromo-4-iodobenzene [29, 30].

We modified the method described by Hazlet [25] and found that bromination of 4-biphenyl tosylate, in chloroform instead of acetic acid as solvent, gives high yields of exclusively 4-bromo-4'-biphenyl tosylate. Thus 4-bromo-4'-hydroxybiphenyl can be prepared in three high yield steps from 4-phenylphenol by tosylation, bromination and hydrolysis. 4-Bromo-4'-hydroxybiphenyl was alkylated with 1-bromohexane, converted into the boronic acid and coupled with 3-bromophenyl acetate to give 4-hexyloxy-3''-hydroxyterphenyl after hydrolysis. The liquid crystal products were then prepared by coupling of the phenols with cholesteryl ω -bromoalkanoates by a method described previously [4, 5]. All compounds were



Scheme 1.



single spot by TLC, and gave NMR spectra in good agreement with their structures and correct elemental analyses.

2.1.1. 4-Bromo-4'-biphenyl tosylate

To a well-stirred, boiling solution of 120 g (0.37 mol) of 4-biphenyl tosylate [31] in 450 ml of dry chloroform was added 2 g of iron powder. Subsequently 21 ml (0.41 mol) of bromine in 50 ml of chloroform was added dropwise. After addition of the first 5 ml of bromine solution, the evolution of HBr started. The rest of the bromine was added at such a rate that a gradual evolution of HBr was maintained. After addition of the bromine, the mixture was heated at reflux for another 4 h until all the bromine was consumed. The solution was cooled, water was added and the organic layer was washed several times with water. The organic layer was dried with sodium sulphate and filtered. The filtrate was concentrated and the residue recrystallized from ethanol. Yield 132 g (89%), m.p. 92–94°C.

2.1.2. 4-Bromo-4'-hydroxybiphenyl

A solution of 50 g (0.124 mol) of 4-bromo-4'-biphenyl tosylate and 50 g of NaOH in 500 ml of a 1:1 mixture of water and ethanol was heated at reflux for 6 h. After cooling, 500 ml of water was added and the solution was washed twice with 200 ml of ether. The aqueous solution was acidified with 90 ml of concentrated HCl

in 100 ml of water and shaken three times with 150 ml of ether. The combined ether extracts were dried with sodium sulphate and concentrated. Yield 29 g (96%), m.p. 165°C after recrystallization from petroleum ether 60-80/chloroform or ethanol/water.

2.1.3. 4-Bromo-4'-hexyloxybiphenyl

A mixture of 5 g (20 mmol) of 4-bromo-4'-hydroxybiphenyl, 3.8 g (23 mmol) of 1-bromohexane and 5 g of potassium carbonate in 50 ml of butanone was heated at reflux for 16 h. After cooling, the mixture was concentrated and purified by column chromatography on silica gel with dichloromethane as eluent. Yield 4.4 g (66%), m.p. 101–102°C. ¹H NMR: (CDCl₃) δ 7.7–7.4 (6H, Ar), 6.9 (2H, Ar), 4.0 (t, 2H, OCH₂), 1.8 (m, 2H), 1.5–1.3 (6H), 0.9 (t, 3H, CH₃).

2.1.4. 4-Hexyloxybiphenyl-4'-ylboronic acid

To a solution of 4.4 g of 4-bromo-4'-hexyloxybiphenyl (13.2 mmol) in 20 ml of dry THF at –78°C was added dropwise 9 ml of a 1.6M solution of butyllithium in hexane (14.4 mmol). After 2.5 h at –78°C, 5.0 g of triisopropyl borate (26.6 mmol) in 20 ml of dry THF was added dropwise at –78°C. The mixture was allowed to warm to room temperature overnight. The mixture was stirred with 20 ml of a 10% HCl solution for 1 h at room temperature and shaken twice with 50 ml of diethyl ether. The combined organic extracts were washed with

water, dried with sodium sulphate and concentrated. The residue was triturated with hexane and filtered. Yield 2.2 g (56%), m.p. 156°C. $^1\text{H NMR}$: (CDCl_3) δ 7.7 (2H, Ar), 7.5 (4H, Ar), 6.9 (2H, Ar), 3.9 (t, 2H, OCH_2), 1.7 (m, 2H), 1.4–1.3 (6H), 0.9 (t, 3H, CH_3). $^{13}\text{C NMR}$: (CDCl_3) δ 159.2, 142.8, 134.5, 133.7, 128.4, 115.1, 68.5, 31.9, 29.5, 26.0, 22.9, 14.2.

2.1.5. 4-Hexyloxy-3''-hydroxyterphenyl

A solution of 2.2 g of 4-hexyloxybiphenyl-4'-ylboronic acid (7.4 mmol) in 10 ml of ethanol was added to a mixture of 1.5 g (7 mmol) of 3-bromophenyl acetate and $\text{Pd}(\text{PPh}_3)_4$ (300 mg) in 20 ml of benzene and 15 ml of aqueous 2M sodium carbonate under a nitrogen atmosphere. The mixture was stirred and heated at reflux for 6 h. After cooling, brine was added and the mixture was shaken with dichloromethane. The combined organic extracts were concentrated and the resulting crude ester was hydrolysed by adding 20 ml of a 2M KOH solution in water/ethanol 1:1 and heating at reflux for 4 h. The reaction mixture was acidified with HCl and the product extracted into dichloromethane. The organic layers were dried with sodium sulphate, concentrated, and the residue triturated with hexane and filtered. Yield 2.2 g (88%), m.p. 207–208°C. $^1\text{H NMR}$: ($\text{CDCl}_3/\text{CD}_3\text{OD}$) δ 7.6 (s, 4H, Ar), 7.5 (d, 2H, Ar), 7.2 (t, 1H, Ar), 7.1 (2H, Ar), 6.9 (d, 2H, Ar), 6.8 (d, 1H, Ar), 3.9 (t, 2H, OCH_2), 1.8 (m, 2H), 1.5–1.2 (m, 6H), 0.9 (t, 3H, CH_3). $^{13}\text{C NMR}$: ($\text{CDCl}_3/\text{CD}_3\text{OD}$) δ 159.1, 157.4, 142.5, 140.0, 139.6, 134.4, 133.6, 130.1, 128.3, 128.2, 127.6, 127.1, 126.1, 118.7, 115.1, 114.5, 114.1, 68.5, 31.8, 29.5, 25.9, 22.8, 14.1.

2.1.6. 4-Hexyloxy-3'-hydroxybiphenyl

A solution of 2.2 g of 4-hexyloxyphenylboronic acid [24] (10 mmol) in 8 ml of ethanol was added to a mixture of 1.72 g (8 mmol) of 3-bromophenyl acetate and $\text{Pd}(\text{PPh}_3)_4$ (300 mg) in 15 ml benzene and 15 ml of aqueous 2M sodium carbonate under a nitrogen atmosphere. The mixture was stirred and heated at reflux for 2 h. After cooling, brine was added and the product extracted into dichloromethane. The combined organic layers were concentrated and the resulting crude ester was hydrolysed by adding 50 ml of 2M KOH in water/ethanol 1:1 and heating at reflux during 4 h. The reaction mixture was acidified with HCl and shaken with diethyl ether. The organic layers were dried with sodium sulphate, concentrated, and the residue was triturated with hexane and filtered. Yield 1.9 g (70%), m.p. 89–90°C. $^1\text{H NMR}$: (CDCl_3) δ 7.5 (d, 2H, Ar), 7.3 (m, 1H, Ar), 7.1 (m, 1H, Ar), 7.0 (2H, Ar), 6.7 (d, 1H, Ar), 4.0 (t, 2H, OCH_2), 1.8 (m, 2H), 1.5–1.2 (m, 6H), 0.9 (t, 3H, CH_3). $^{13}\text{C NMR}$: (CDCl_3) δ 158.8, 155.8, 142.7, 133.0, 128.1, 119.3, 114.8, 113.6, 113.5, 68.2, 31.6, 29.3, 25.8, 22.7, 14.1.

2.1.7. Cholesteryl 11-(4''-hexyloxyterphenyl-3-ox y)-undecanoate III-10

A mixture of 1 mmol of 4-hexyloxy-3''-hydroxyterphenyl, 1.1 mmol of cholesteryl 11-bromoundecanoate [5] and 1 g of anhydrous potassium carbonate in 20 ml of butanone was heated at reflux for 16 h. The solvent was evaporated and the residue treated with 20 ml of dichloromethane. The solid material was filtered and washed with another 20 ml of dichloromethane. The filtrate was concentrated and the residue purified by column chromatography on silica gel with petroleum ether 40–60/dichloromethane 1:1 as eluent and recrystallized from butanone, yield 80%. $^1\text{H NMR}$: (CDCl_3) δ 7.6–7.5 (6H, s and d, Ar), 7.3 (1H, t, Ar), 7.2 (2H, Ar), 7.0 (2H, d, Ar), 6.9 (1H, dd, Ar), 5.4 (1H, m, =CH), 4.6 (1H, m, CHO), 4.0 (4H, $2 \times \text{CH}_2\text{O}$), 2.3–0.6 (72H, aliphatic). Anal: found, C 82.99, H 10.25; calc. for $\text{C}_{62}\text{H}_{90}\text{O}_4$, C 82.80, H 10.09%.

The other dimer liquid crystals were prepared similarly starting from the appropriate phenolic derivative and a cholesteryl ω -bromoalkanoate.

2.2. Measurements

Determination of melting points and thermal phase transition temperatures and optical inspection of the liquid crystalline phases were carried out on samples mounted between glass slides using an Olympus BH-2 polarizing optical microscope equipped with a Mettler FP82HT hot stage, controlled by a Mettler FP80HT central processor. Temperature dependent transmission spectra of the chiral nematic phases of the compounds were recorded by inserting the hot stage with the sample between parallel glass slides into the measuring beam of a Hewlett Packard 8452A diode array spectrophotometer. Differential scanning calorimetry (DSC) thermograms were obtained on a Perkin Elmer DSC-7 system. The entropy changes at the phase transition temperatures are expressed as $\Delta S/R$, in which ΔS is calculated from $\Delta S = \Delta H/T$. ΔH is calculated in J mol^{-1} and T is the corresponding phase transition temperature in Kelvin. X-ray diffraction on the samples was measured by employing a Siemens Histar area detector using monochromatic CuK_α radiation. The temperature was controlled by an oven built in-house.

3. Results and discussion

3.1. Thermotropic properties

The thermotropic properties of the series **I-n** are given in the table and are depicted in figure 1. All compounds in this series form enantiotropic liquid crystals with chiral nematic mesophases. Except for **I-6**, all the compounds also exhibit a smectic A phase. Polarization microscopy showed either focal-conic or featureless homeotropic textures for these phases and X-ray reflection

Table. Transition temperatures ($^{\circ}\text{C}$) and (in parentheses) reduced transition entropies $\Delta S/R$ for LC dimers **I-n**, **II-n** and **III-n**.

| Compound | M.p. | SmA-N* | N*-I | SmA-I |
|--------------------------|------|------------|------------|-----------|
| I-3 | 160 | 198 (0.28) | 207 (1.15) | — |
| I-4 | 127 | 133 (0.17) | 148 (0.40) | — |
| I-5 | 136 | 162 (0.12) | 181 (1.20) | — |
| I-6^a | 103 | — | 123 (0.34) | — |
| I-7 | 110 | 161 (0.65) | 168 (1.52) | — |
| I-10^a | 95 | 130 (0.64) | 138 (0.67) | — |
| II-3 | 58 | — | 19 (0.09) | — |
| II-4 | 82 | — | — | 59 (2.1) |
| II-5 | 47 | — | 33 (0.11) | — |
| II-6 | 66 | — | 36 (0.65) | — |
| II-7 | 54 | — | 33 (0.22) | — |
| II-10^a | 63 | — | 42 (0.81) | — |
| III-3 | 120 | — | — | 112 (2.0) |
| III-4 | 113 | — | — | 153 (2.9) |
| III-5 | 107 | — | — | 117 (1.6) |
| III-6 | 101 | — | — | 139 (2.6) |
| III-7 | 88 | — | — | 115 (1.7) |
| III-10 | 94 | — | — | 124 (2.8) |

^a These compounds may exist in other crystalline forms with lower melting points: **I-6** 96°C , **I-10** 72°C , **II-10** 48 and 58°C .

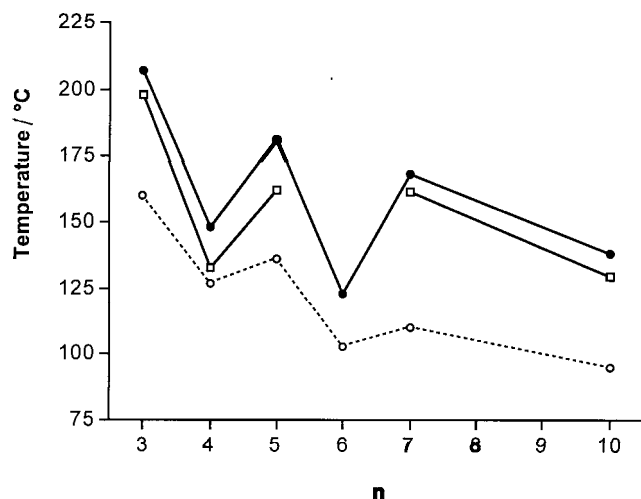


Figure 1. Dependence of the melting points (—○—), SmA-N* (—□—) and N*-I transition temperatures (—■—) of the compounds of series **I-n** on the number of methylene groups n in the spacers.

showed one or two peaks in the small angle region and a diffuse peak in the large angle region, indicative of SmA ordering.

The observed alternations in the isotropization temperatures are very similar to those observed previously for dimers with cholesterol and cyanobiphenyl as mesogenic units [4, 5]. For these compounds, however, the chiral nematic phase window became wider with increasing spacer length, while for compounds **I-n** a

rather small chiral nematic phase window is observed. An exception is compound **I-6**, which remains nematic even when cooled to about 70°C , when crystallization of the sample occurs. For non-symmetrical dimers containing two aromatic mesogenic units, it has been found that two different SmA modifications can exist depending on the length of the spacer and the terminal alkyl chain [2, 3, 32, 33]. For a certain length of terminal alkyl group and shorter spacers an interdigitated SmA (SmA_d) phase was found, with a smectic layer spacing d of ≥ 1.5 times the length of the molecule l , while for longer spacers an intercalated SmA (SmA_c) phase was observed with a d/l ratio of about 0.5. When spacer and terminal alkyl chain lengths were about equal, neither smectic modification was favourable; the smectic behaviour disappeared and only a nematic phase was found. The change in smectic ordering was found for non-symmetric dimers with two polarizable aromatic mesogenic units, and favourable specific interactions between the unlike mesogenic units were held responsible for this behaviour.

For dimers with cholesteryl moieties, however, slightly different behaviour was found [34–38]. Depending on spacer and terminal alkyl chain length, two different smectic modifications were also observed. The smectic layer spacing observed by X-ray diffraction indicated intercalated smectic phases with a d/l ratio of about 0.5 when the spacer is short, and smectic phases with a d/l ratio of about 1 when the spacer is longer than the alkyl terminal chain. When spacer and terminal alkyl groups were about equal, so-called incommensurate or frustrated smectic phases were often found. With strong electron withdrawing groups at the end of the aromatic mesogenic unit, interdigitated phases were recently found with a d/l ratio of about 1.5 [39].

X-ray diffraction studies of compounds **I-7** and **I-10** show layer spacings of 22 and 23 Å, respectively. With lengths of the molecules in their most elongated conformations of about 46 and 49 Å as estimated from molecular models, a d/l ratio of about 0.5 can be calculated. For **I-4** and **I-5**, layer spacings of 43 and 44 Å, respectively, are observed; with an estimated length of the molecules of 43 and 44 Å, a d/l ratio of about 1 is obtained. This corresponds well with the behaviour found previously for cholesteryl-containing dimers [35]. However, the fact that no smectic phase was found for **I-6** causes these compounds to deviate slightly from the behaviour of the compounds investigated by Hardouin *et al.* [34–37]. The different SmA orderings of the compounds in this series was also evidenced by the transition from SmA to N* as judged by polarizing optical microscopy. For the shorter spacers, the transition from SmA to N* was preceded by the growth of curved lines in a homeotropic sample, whereas for longer spacers the transition was abrupt and no growth of curved lines

was found. The formation of these lines in the homeotropic SmA phase is probably related to an intermediate twist grain boundary (TGBA) phase [40, 41]. In this respect it is also noteworthy that the total change in $\Delta S/R$ at the SmA–N* transition for the compounds with the shorter spacers is significantly smaller than that for the compounds with the longer spacers (see the table). It has been suggested that a small change in $\Delta S/R$ at the SmA–N* transition is a prerequisite for obtaining TGBA phases [40]. It is also noteworthy that the compounds with a small N*–I transition enthalpy (**I-4** and **I-6**) show the typical platelet texture of blue phases upon slow cooling from the isotropic melt [7]. We did not attempt to determine the separate transitions involving the blue phases or the TGBA phases by DSC, because no well separated peaks were obtained.

The thermotropic properties of the dimers **II-*n*** are given in the table and depicted in figure 2. All the compounds of this series show only monotropic behaviour and are chiral nematic, except **II-4** which is smectic. X-ray diffraction (figure 3) indicates that this compound probably exhibits a SmA phase with a layer spacing corresponding to a d/l ratio of about 1 ($d = 40 \text{ \AA}$ and l is about 42 \AA). Why only this compound of the series is SmA is unclear. Perhaps the length of the spacer and the terminal alkyl group are such that they nicely fill the available space in a smectic arrangement. Perhaps this is also the reason for the rather high isotropization temperature of this compound.

The observed alternation of the melting points and the isotropization transitions with n is reversed as compared with compounds **I-*n***. From figures 1 and 2, it can also be seen that both the melting points and the

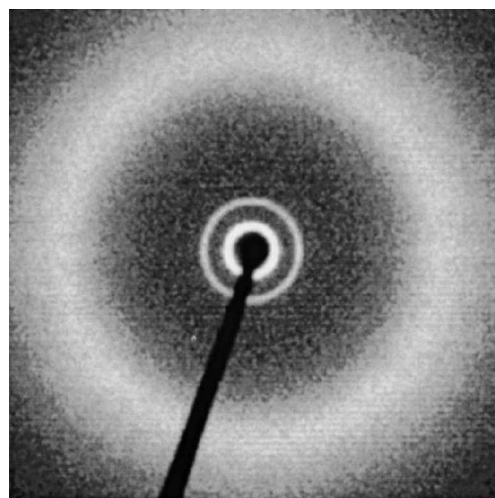


Figure 3. X-ray micrograph of compound **II-4** obtained at 60°C . A strong reflection is found at 41 \AA and a weaker reflection at 20 \AA .

isotropization temperatures are considerably lower in compounds **II-*n*** with the *meta*-attachment. Due to the *meta*-attachment the molecules have a kink and therefore do not pack easily in crystals and liquid crystals and consequently these phases form at lower temperatures.

Because the compounds of series **II-*n*** form monotropic liquid crystals and do not have a comparable isotropization transition, we decided to prepare also the terphenyl analogues of compounds **II-*n***. The melting points and isotropization temperatures of these compounds are given in the table and depicted in figure 4. All compounds show enantiotropic liquid crystalline behaviour, except **III-3**, which is monotropic. Only SmA phases are found and X-ray diffraction reveals a smectic layer spacing corresponding to a d/l ratio of about 0.5

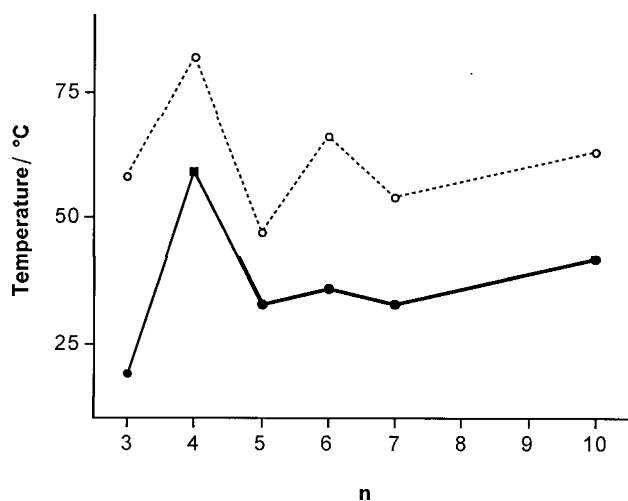


Figure 2. Dependence of the melting points (---○---) and isotropization temperatures (—■—) of the compounds of series **II-*n*** on the number of methylene groups n in the spacers.

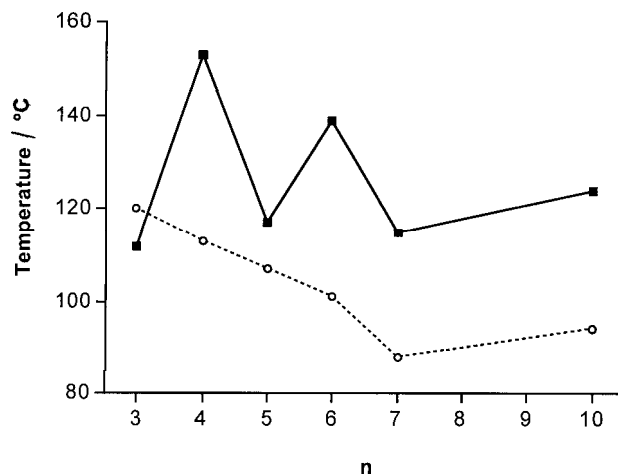


Figure 4. Dependence of the melting points (---○---) and SmA–I transition temperatures (—■—) of the compounds of series **III-*n*** on the number of methylene groups n in the spacers.

for all compounds of the series (for example for **III-6**, d is 23 Å and l is about 46 Å). The alternation of the liquid crystal to isotropic transitions with n is very clear and follows the same inverse trend as that found for compounds **II- n** . The trend in the melting points of compounds **III- n** does not suggest an odd–even effect.

In figure 5 the reduced entropy changes $\Delta S/R$ of the isotropization transitions of all three series of compounds are depicted. This figure clearly shows that for all three series, $\Delta S/R$ alternates with spacer parity and that the alternation is reversed for series **II- n** and **III- n** as compared with series **I- n** . For each series the higher entropy changes also correspond to higher transition temperatures and higher ordering in the mesophases. The relatively high $\Delta S/R$ value of compound **II-4** is due to a SmA–I transition for this compound, whereas the rest of the series exhibit N*–I transitions. For compounds **III- n** , the $\Delta S/R$ values are higher than for the other series. This is because all transitions for this series are SmA–I and the aromatic moiety is a terphenyl unit instead of the poorer mesogenic biphenyl unit in series **I- n** and **II- n** .

The inverse alternation observed for series **II- n** and **III- n** , as compared with series **I- n** , indicates a better ordering of the compounds in series **II- n** and **III- n** when the spacer connecting the mesogenic units is odd (even n –CH₂– + 2 –O– + 1 C=O) than when the spacer is even. This means that the bent orientation of the attachment of the spacer to the aromatic core helps in attaining a better ordering if an odd spacer is present. Schematically this can be depicted as in figure 6, where the influence of angle of attachment and parity of the spacer on ordering are illustrated.

Based on these simple models, the change in odd–even alternation can be visualized. However, when only series **I- n** and **II- n** are compared, it is seen that the compounds in series **II- n** are much poorer liquid crystals, with isotropization temperatures that are often more than 100°C lower than those of compounds **I- n** . This may be caused by the increased number of conformations that are possible for compounds **II- n** due to rotation about the spacer–biphenyl bond, of which many are not ideal for liquid crystalline behaviour, i.e. parallel alignment of the mesogenic units (see figure 7). For the

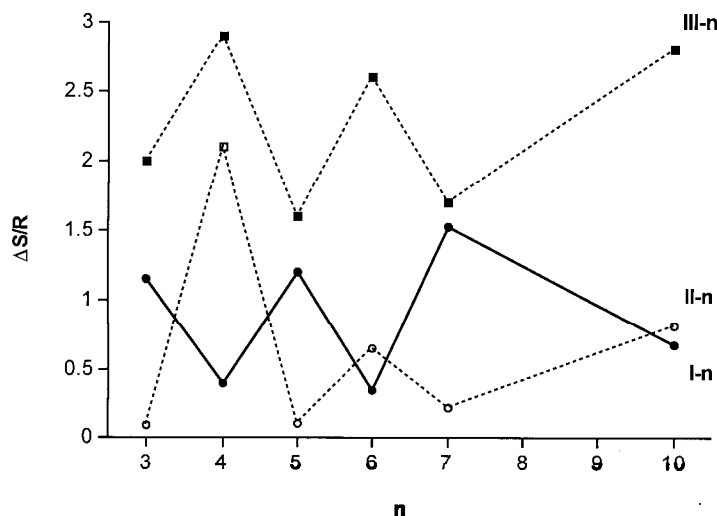


Figure 5. Dependence of the entropy change $\Delta S/R$ of the isotropization transitions of the compounds of series **I- n** , **II- n** and **III- n** on the number of methylene groups n in the spacers (circles: N*–I transitions and squares: SmA–I transitions).

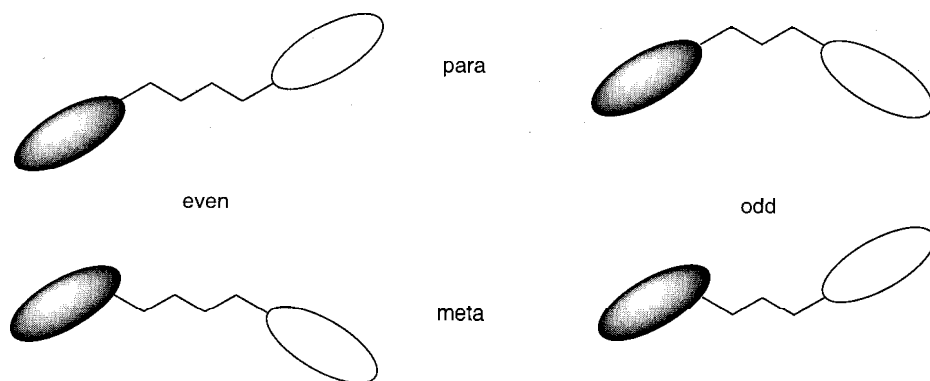


Figure 6. Simple model to visualize the effect of spacer parity and *meta*- or *para*-attachment on the ordering of liquid crystal dimers.

Figure 7. Influence of rotation of the mesogenic group around a *meta*-bond to the spacer on the ordering.



para-substituted mesogenic units, such a rotation around the spacer–biphenyl bond does not give different conformations, and consequently more conformations are possible with parallel orientations of the mesogenic units. The terphenyl unit of compounds **III-n** is a better mesogenic group due to its longer shape and now transition temperatures in the same range as for the compounds **I-n** are found.

3.2. Optical properties

Aligned chiral nematic phases exhibit a helical ordering which can selectively reflect circularly polarized light of a certain wavelength. It has been shown that for chiral dimer liquid crystals, the selective reflection wavelength strongly depends on the parity of the spacer [4–8]. For the better ordered dimers a higher selective reflection wavelength is found. When the dimers are in solution in another chiral nematic phase, the selective reflection wavelength is affected similarly. In this way it is also possible to investigate the ordering properties of the dimers, even if not all compounds of a series have a chiral nematic phase.

For compounds **I-n** the selective reflection wavelengths of the better ordered pure compounds **I-3**, **I-5** and **I-7** are found at about 600 nm and for the poorer ordered compounds **I-4**, **I-6** and **I-10** at about 400 nm. These findings compare well with results previously found for dimers with cholesteryl and cyanobiphenyl groups [4, 5]. For the compounds of series **II-n**, only selective reflection wavelengths for compounds **II-6** and **II-10** could be measured. At room temperature the selective reflection wavelengths of these compounds are found at about 380 nm.

For the present three series of compounds, the selective reflection wavelength as a function of spacer length was also measured for a 5 wt % solution in a host consisting of a 1:2 mixture by weight of cholesteryl chloride and cholesteryl nonanoate at room temperature. The change in the selective reflection wavelength caused by 5 wt % of the guest is given in figure 8. The screw sense of the host is the same as the screw sense of the guest and a selective reflection of the host used of 630 nm is found.

It is clearly seen that the alternation of the properties with n for the two series **II-n** and **III-n** is reversed compared with that of series **I-n**. The changes observed for series **I-n** are somewhat larger than for the other series. For compounds **I-n** with odd n , the number of flexible units between the mesogenic groups is even, and

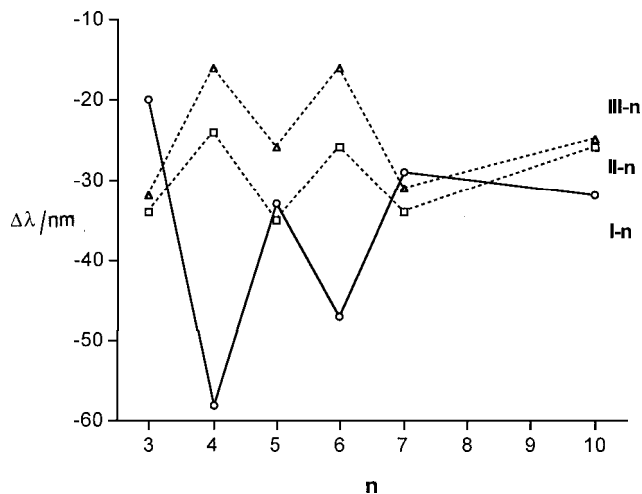


Figure 8. Induced change in selective reflection wavelength $\Delta\lambda$ (nm) at room temperature brought about by a 5 wt % solution of compounds **I-n**, **II-n** and **III-n** in a cholesteric host consisting of a 2:1 (w/w) mixture of cholesteryl nonanoate and cholesteryl chloride as a function of n .

a better ordered chiral nematic phase with a higher selective reflection wavelength is expected than for compounds **I-n** with even n . This was confirmed by measurements on the pure compounds. Mixed with the host, a smaller decrease in selective reflection wavelength is therefore expected for compounds **I-n** with odd n . This is indeed found. For series **II-n** and **III-n**, the influence of the guests on the host as a function of n is reversed. This is in agreement with the predictions.

4. Conclusions

We have clearly shown that in dimer liquid crystals, the angle between the long axis of the mesogenic group and the bond connecting the mesogenic unit with the spacer is important for the ordering of the resulting liquid crystals. When the spacer is connected at a *para*-position of the mesogenic unit, the angle is approximately zero and compounds are obtained with relatively high transition temperatures and the dimers show an odd–even effect in their mesogenic properties as a function of spacer length; the compounds with an even number of flexible units between the mesogenic groups exhibit higher isotropization temperatures, higher associated enthalpy effects and higher selective reflection wavelengths of the chiral nematic phases. When the spacer is connected to the mesogenic group at a *meta*-position, the transition temperatures of the resulting dimers are

much lower. Now the dimers exhibit an odd–even effect in their mesogenic properties as a function of spacer length that is reversed; the compounds that have an even number of flexible units between the mesogenic units have lower isotropization temperatures, lower associated enthalpy effects and lower helical twisting power than the compounds with an odd spacer. For these compounds more conformers in the liquid crystalline phase are expected with a parallel orientation of the mesogenic units when the spacer connecting them is odd. When the mesogenic core of such compounds is extended as in the terphenyl compounds, materials are obtained that are good liquid crystals.

We would like to thank Dr E. Klop and Prof. Dr S. J. Picken from AKZO Nobel Research Arnhem for the use of X-ray equipment to measure the layer spacings of the smectic liquid crystals.

References

- [1] LUCKHURST, G. R., 1995 *Macromol. Symp.*, **96**, 1.
- [2] IMRIE, C. T., and LUCKHURST, G. R., 1998, *Handbook of Liquid Crystals*, Vol. 2B, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill (Weinheim: Wiley-VCH), p. 801.
- [3] IMRIE, C. T., 1999, *Structure and Bonding*, **95**, 150.
- [4] MARCELIS, A. T. M., KOUDELS, A., and SUDHÖLTER, E. J. R., 1994, *Recl. Trav. Chim. Pays-Bas*, **113**, 524.
- [5] MARCELIS, A. T. M., KOUDELS, A., and SUDHÖLTER, E. J. R., 1995, *Liq. Cryst.*, **18**, 843.
- [6] MARCELIS, A. T. M., KOUDELS, A., and SUDHÖLTER, E. J. R., 1995, *Liq. Cryst.*, **18**, 851.
- [7] BLATCH, A. E., FLETCHER, I. D., and LUCKHURST, G. R., 1997, *J. mater. Chem.*, **7**, 9.
- [8] MARCELIS, A. T. M., KOUDELS, A., and SUDHÖLTER, E. J. R., 1996, *J. mater. Chem.*, **6**, 1469.
- [9] MARCELIS, A. T. M., KOUDELS, A., and SUDHÖLTER, E. J. R., 1996, *Liq. Cryst.*, **21**, 87.
- [10] MARCELIS, A. T. M., KOUDELS, A., and SUDHÖLTER, E. J. R., 1996, *Thin Solid Films*, **284–285**, 308.
- [11] BARNES, P. J., DOUGLASS, A. G., HEEKS, S. K., and LUCKHURST, G. R., 1993, *Liq. Cryst.*, **13**, 603.
- [12] ABE, A., FURUYA, H., NAM, S. Y., and OKAMOTO, S., 1995, *Acta Polym.*, **46**, 437.
- [13] WEISSFLOG, W., 1998, *Handbook of Liquid Crystals*, Vol. 2B, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill (Weinheim: Wiley-VCH), p. 835.
- [14] WEISSFLOG, W., and DEMUS, D., 1988, *Liq. Cryst.*, **3**, 275.
- [15] LEE, J.-W., PIAO, X. L., YUN, Y.-K., JIN, J.-I., KANG, Y.-S., and ZIN, W.-C., 1999, *Liq. Cryst.*, **26**, 1671.
- [16] WEISSFLOG, W., DEMUS, D., DIELE, S., NITSCHKE, P., and WEDLER, W., 1989, *Liq. Cryst.*, **5**, 111.
- [17] HUH, S.-M., JIN, J.-I., ACHARD, M. F., and HARDOUIN, F., 1998, *Liq. Cryst.*, **25**, 285.
- [18] PELZL, G., DIELE, S., and WEISSFLOG, W., 1999, *Adv. Mater.*, **11**, 707.
- [19] SHEN, D., DIELE, S., PELZL, G., WIRTH, I., and TSCHERSKE, C., 1999, *J. mater. Chem.*, **9**, 661.
- [20] SEKINE, T., NIORI, T., SONE, M., WATANABE, J., CHOI, S.-W., TAKANISHI, Y., and TAKEZOE, H., 1997, *Jpn. J. appl. Phys.*, **36**, 6455.
- [21] WATANABE, J., NIORI, T., CHOI, S.-W., TAKANISHI, Y., and TAKEZOE, H., 1998, *Jpn. J. appl. Phys.*, **37**, L401.
- [22] CHOI, S.-W., ZENNYOJI, M., TAKANISHI, Y., TAKEZOE, H., NIORI, T., and WATANABE, J., 1999, *Mol. Cryst. liq. Cryst.*, **328**, 185.
- [23] NIEUWHOF, R. P., MARCELIS, A. T. M., SUDHÖLTER, E. J. R., PICKEN, S. J., and DE JEU, W. H., 1999, *Macromolecules*, **32**, 1398.
- [24] GOODBY, J. W., HIRD, M., LEWIS, R. A., and TOYNE, K. J., 1996, *J. chem. Soc. chem. Commun.*, 2719.
- [25] HAZLET, S. E., 1937, *J. Am. chem. Soc.*, **59**, 1087.
- [26] HSU, C. S., RODRIGUEZ-PARADA, J. M., and PERCEC, V., 1987, *J. polym. Sci. A*, **25**, 2425.
- [27] RODENHOUSE, R., PERCEC, V., and FEIRING, A. E., 1990, *J. polym. Sci. C*, **28**, 345.
- [28] GRAY, G. W., HARTLEY, J. B., and JONES, B., 1952, *J. chem. Soc.*, 1959.
- [29] PLEHNERT, R., SCHRÖTER, J. A., and TSCHERSKE, C., 1998, *J. mater. Chem.*, **8**, 2611.
- [30] ANDERSCH, J., TSCHERSKE, C., DIELE, S., and LOSE, D., 1996, *J. mater. Chem.*, **6**, 1297.
- [31] HAZLET, S. E., 1937, *J. Am. chem. Soc.*, **59**, 287.
- [32] ATTARD, G. S., DATE, R. W., IMRIE, C. T., LUCKHURST, G. R., ROSKILLY, S. J., SEDDON, J. M., and TAYLOR, L., 1994, *Liq. Cryst.*, **16**, 529.
- [33] DATE, R. W., IMRIE, C. T., LUCKHURST, G. R., and SEDDON, J. M., 1992, *Liq. Cryst.*, **12**, 203.
- [34] HARDOUIN, F., ACHARD, M. F., JIN, J.-I., SHIN, J.-W., and YUN, Y.-K., 1994, *J. Phys. II Fr.*, **4**, 627.
- [35] HARDOUIN, F., ACHARD, M. F., JIN, J.-I., and YUN, Y.-K., 1995, *J. Phys. II Fr.*, **5**, 927.
- [36] HARDOUIN, F., ACHARD, M. F., JIN, J.-I., YUN, Y.-K., and CHUNG, S.-J., 1998, *Eur. Phys. J.*, **B1**, 47.
- [37] HARDOUIN, F., ACHARD, M. F., LAGUERRE, M., JIN, J.-I., and KO, D.-H., 1999, *Liq. Cryst.*, **26**, 589.
- [38] CHA, S.-W., JIN, J.-I., LAGUERRE, M., ACHARD, M. F., and HARDOUIN, F., 1999, *Liq. Cryst.*, **26**, 1325.
- [39] LEE, D. W., JIN, J.-I., LAGUERRE, M., ACHARD, M. F., and HARDOUIN, F., 2000, *Liq. Cryst.*, **27**, 145.
- [40] GOODBY, J. W., 1999, *Structure and Bonding*, **95**, 83.
- [41] DIERKING, I., and LAGERWALL, S. T., 1999, *Liq. Cryst.*, **26**, 83.