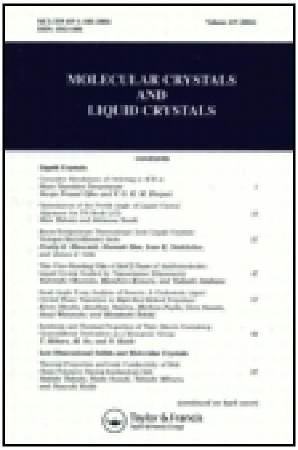

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SMECTIC C PHASES AND REENTRANT BEHAVIOR IN CHOLESTEROL CONTAINING DIMER LIQUID CRYSTALS

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A series of dodecyloxybiphenylyl and cholesteryl group containing dimers with ethers as spacers have been prepared and their liquid crystalline properties were investigated as a function of spacer length. For short spacers SmA and SmC phases were observed with monolayer ordering. This is aparent from polarization microscopy and temperature dependent X-ray measurements. With increasing spacer length a N-phase gradually appears whose liquid crystalline range increases. For the dodecyl spacer no smectic phase is observed anymore. For the nonyl spacer reentrant behavior is found (N*-TGB-SmA-TGB-N*). Reentrant behavior, probably N*-TGB-N*, is also observed for a related compound with an ester spacer.*

Keywords: chiral nematic; cholesteric; smectic A; smectic ordering; twist grain boundery; X-ray

INTRODUCTION

Dimer liquid crystals form a class of liquid crystals in which two mesogenic units are connected by a flexible spacer. These compounds show several intriguing properties [1,2]. They exhibit a strong odd – even effect in the phase transitional properties depending on the parity of the spacer. Another interesting phenomenon of dimer liquid crystals with smectic phases is the variation found in the smectic layer spacings [1–5].

For unsymmetrical dimers with cholesteryl moieties, three different smectic modifications were observed, depending on spacer, type of

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aromatic mesogen and terminal alkyl chain length [6–10]. The smectic layer spacing observed with X-ray diffraction indicates intercalated smectic phases with a d/l ratio of about 0.5 when the spacer is longer and smectic phases with a d/l ratio of about 1 when the spacer is shorter than the alkyl terminal chain. When spacer and terminal alkyl groups are about equal, so-called incommensurate or frustrated smectic phases are sometimes found, or no smectic behavior at all. Recently, interdigitated phases with a d/l ratio of about 1.5 were found for cholesteryl dimers with electron-withdrawing groups at the end of the aromatic mesogenic unit [8,10].

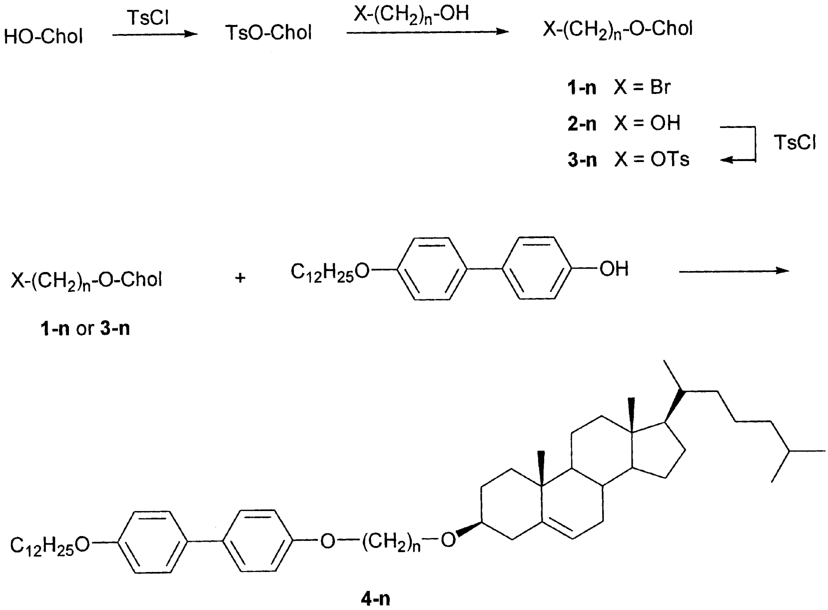
For a series of pentyloxy- and hexyloxybiphenylyl and cholesteryl containing dimer liquid crystals that we recently investigated, we observed monolayer SmA phases for spacer lengths shorter than nine and intercalated SmA phases for spacer lengths longer than nine flexible units, and only nematic behavior for compounds with a spacer length of nine flexible units. For the butyloxybiphenylyl compounds those with more than seven flexible units in the spacer had an intercalated SmA phase, and two compounds (with seven and nine flexible units in the spacer) had only nematic phases [10].

The cholesteryl and alkoxybiphenylyl mesogenic groups in the dimer liquid crystals are very different. One group is aromatic, while the other is not. Furthermore, the cross-sectional area of the cholesterol group is much larger than that of the biphenylyl group and also the terminal alkyl group of the cholesterol group is branched. Therefore it is not easy to predict the effect of increasing the terminal alkyl group of the biphenylyl unit on the liquid crystalline properties of the dimers. Based on our previous findings and those of others [4–10], several things could be expected. It is likely that the monolayer ordering of the smectic phase will also be found for longer spacers, but also that with longer spacers the nematic phase will become more important. It has also been observed that increasing the terminal alkyl length in dimers can lead to smectic polymorphism.

In order to investigate this we prepared a series of dodecyloxybiphenylyl and cholesteryl containing dimers and studied their liquid crystalline properties. We used alkyl spacers with a number of methylene groups ranging from 4 to 12, connected to the mesogenic units via ether linkages.

RESULTS AND DISCUSSION

The syntheses of the compounds is depicted in the following Scheme.



SCHEME Synthesis of the dimer liquid crystals **4–n**

We used ethers because of the commercial availability of a long range of alkanediols or bromoalkanols. Cholesteryl tosylate was reacted for 24 h with an 6-fold excess of diol or bromoalkanol in refluxing dioxane to give the bromides **1-n** or the alkohols **2-n** in 70–80% yield [11]. Alkohols **2-n** were then converted into the tosylates **3-n**. Finally, reaction of the bromides or the tosylates with dodecyloxybiphenol during 1 or 2 days in refluxing butanone with potassium carbonate as a base gave the dimer liquid crystals **4-n** in good yield.

The liquid crystalline properties were determined with optical polarizing microscopy, DSC and X-ray analysis. The phase transition temperatures together with the reduced transition entropies ($\Delta S/R$) are given in the Table. The transition temperatures are also graphically represented in Figure 1.

For short spacers (n = 4–6) only smectic phases were observed and no cholesteric phases. For compounds with longer spacers a cholesteric phase (N^*) is observed whose range increases when the spacer becomes longer. Surprisingly, for n = 4–8 a SmC phase was observed. There are only a few reports on SmC phases of cholesteryl compounds. Some cholesteryl containing dimers with a relatively long terminal alkyl group have been reported to exhibit a SmC-phase [12,13]. The formation of this tilted phase is clearly seen by the development of Schlieren textures with optical

TABLE Phase Transition Temperatures (°C) of the Dimers **4-n**. The Reduced Transition Entropies (ΔS/R) are Given in Brackets

n	Mpt	SmC		SmA			N*	I	
4	103	●	(98)	●				182	[3.20]
5	67	●	78	●				120	[1.88]
6	100	●	113	●				162	[3.22]
7	68	●	79	●	114	[0.81]	●	116	[0.64]
8	89	●	105	●	138	[1.20]	●	143	[1.92]
9	88	●	*90 (N^*_{re}-SmA)*	●	110	[0.34]	●	122	[0.63]
10	126			●	127	[0.37]	●	137	[1.75]
11	113			●	(98	[0.06])	●	120	[0.82]
12	128						●	(125	[1.59])

microscopy upon cooling of a homeotropically aligned SmA film of this material to the SmC phase (Fig. 2).

With DSC this transition is difficult to observe. Figure 3 shows the DSC thermogram of the dimer with spacer n = 8.

The SmA-SmC transition is only observable as a change in heat capacity. When the layer spacing (d) as determined with X-ray is plotted as a function of temperature (Fig. 4) the layer spacing decreases sharply when the

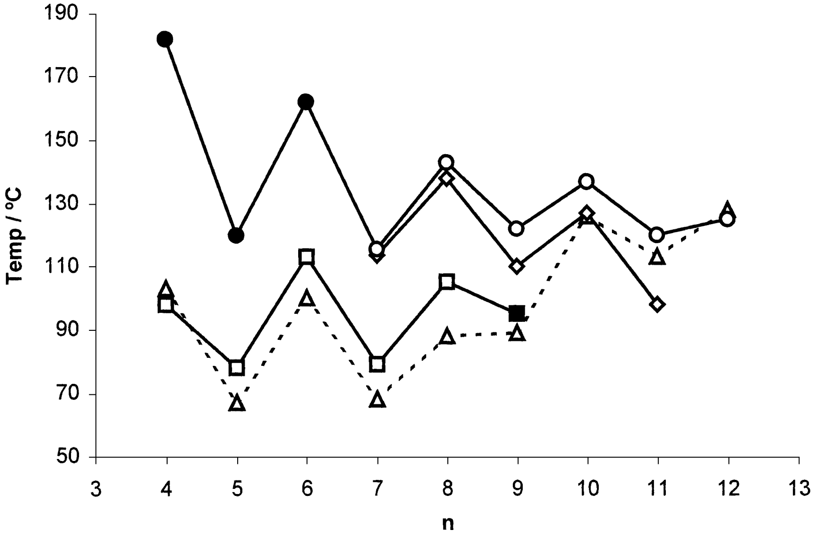


FIGURE 1 Phase transition temperatures of compounds **4-n** as a function of spacer length n. SmA-I (–●–); N*-I (–○–); SmA-N* (–◇–); SmC-SmA (–□–); Cr (–△–); N*re (■).

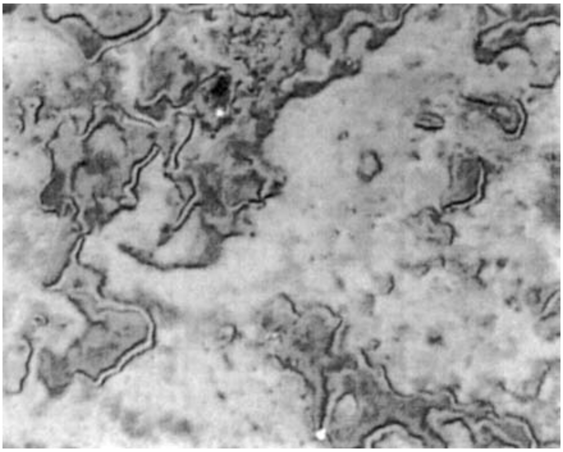


FIGURE 2 Schlieren texture of the SmC phase of compound **4–8** at 90℃.

sample is cooled below the SmA-SmC transition temperature. Such a decrease in layer spacing can be expected when the molecules in the smectic layers become tilted and is typical for a transition from SmA to SmC. We did not yet investigate if the SmC-phase exhibits ferroelectric properties as one would expect from a chiral molecule.

When the layer spacings d of the SmA phases are compared with the calculated molecular length l of the dimers in their most stretched

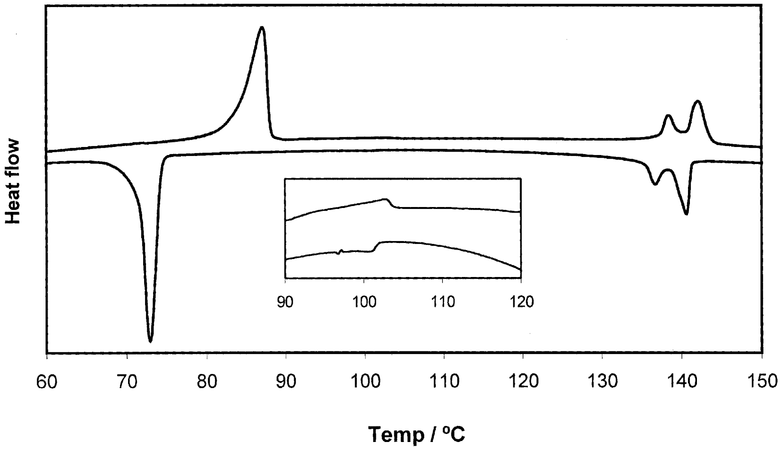


FIGURE 3 DSC traces of a heating and cooling curve of compound **4–8**. The inset is an expansion of the heat flow of the region where the transition from SmC to SmA occurs.

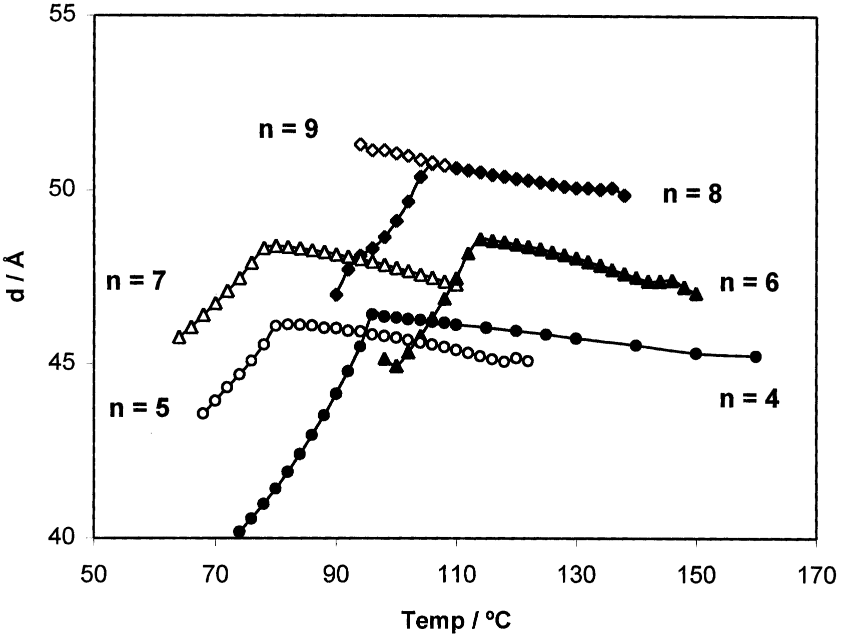


FIGURE 4 Temperature dependence of the smectic layer spacing of compounds **4-n** as obtained from X-ray.

conformation, a d/l ratio of about 1 is found. This can be interpreted as a monolayer smectic ordering. As expected the layer spacing increases with increasing spacer length. An interesting phenomenon is that the layer spacings of the even compounds with spacer n are about equal or even slightly larger than those of the odd compounds with one additional CH_2-group.

In analogy with the alkoxybiphenylyl compounds investigated earlier the monolayer smectic ordering of the SmA phase corresponds to a situation with relatively short spacers and long terminal groups. With increasing spacer length we observed for compounds with a butyloxy to hexyloxy terminal group that at a certain spacer length the smectic ordering disappears and with longer spacers that the smectic phase is restored again, but now the ordering is of an intercalated SmA type [9]. In the present series only monolayer and no intercalated SmA phase is observed, as can be expected for the range of spacers that were investigated. For larger spacers N* phases appear (Fig. 1). For n = 7 a N* phase with a temperature range of 2 degrees is present. For longer spacers the N* range increases. Also for n > 8 the SmC phase is not present anymore. These findings suggest that smectic ordering becomes more difficult when the spacer length approaches the length of the terminal group. For n = 12 no smectic phase is observed anymore, but also the N* liquid crystalline range becomes small, because the isotropization temperature decreases and the melting point increases with spacer length. These findings also make it unlikely that a transition to an intercalated smectic phase with even longer spacers can be observed. All N*-SmA transitions are accompanied by a TGB phase. This is manifested by the development of spiral lines when a homeotropic SmA phase is heated into the N* phase. A peculiar observation was made for compound **4–9**: cooling the homeotropic SmA phase below 95°C also results in the development of spirals and finally in the typical cholesteric texture (Fig. 5).

Therefore this behavior is a reentrant phenomenon. Reentrant behavior is often observed as the result of some frustration [14]. Frustration resulting in incommensurate behavior [6,7] and reentrant behavior [15] has been observed before in cholesteryl containing dimer liquid crystals. However, compounds that exhibit this behavior invariably had a hexanoate spacer. Our results indicate that such behavior is also possible for longer spacers.

Not only compound **4–9** with an ether spacer exibits this reentrant behavior; the related cholesterol containing dimer cholesteryl 11-(4′-dodecyloxybiphenylyloxy)undecanoate also shows reentrant behavior. This compound has a melting point of 116°C and a N*-I transition temperature of 127℃. Upon cooling it is seen that the selective reflection wavelength sharply increases from blue at 112℃ to red at 110℃. This transition also shows up as a small peak in DSC. At about 103℃ the selective reflection wavelength decreases again from red to blue. A good observation of the behavior at still lower temperatures is hampered by crystallization of the sample. Usually, a sharp increase in selective reflection wavelength in related compounds indicates a transition to the TGB phase, soon followed by a transition to the SmA phase. For this compound we assume that a transition to a TGB phase starts, but the SmA phase is not reached and at lower temperature reentrant behavior to the N* phase occurs.

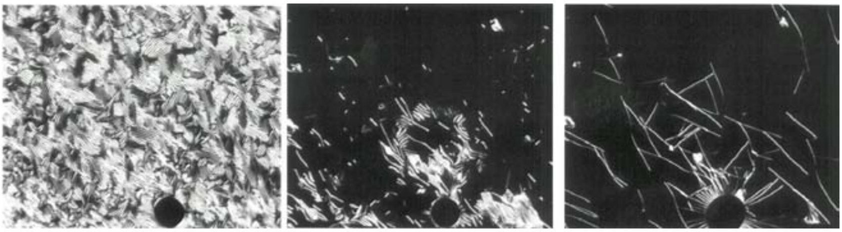


FIGURE 5 Polarizing optical micrographs obtained upon cooling compound **4–9** showing from left to right: many lines at the TGB-SmA transition; largely homeotropic SmA phase and growth of lines at reentrant SmA-TGB transition.

Concluding, long terminal groups in cholesteryl biphenylyl dimers induce SmC phases for short spacers and a monolayer smectic ordering. For longer spacers the smectic phases are destabilized and the nematic range increases. For certain spacers with a length about equal to the terminal group length reentrant behavior resulting from frustration can be obtained. This was also found for a related dimer with an ester as a spacer.

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