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Cholesterol-containing liquid crystal dimers with ether linkages between the spacer and mesogenic units

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Three series of chiral liquid crystalline dimers were investigated, having a cholesteryl and a cyanobiphenylyl, butoxybiphenylyl or hexyloxybiphenylyl group connected to a variable alkyl spacer through ether linkages. Their properties were compared with those of the corresponding ester derivatives. The phase behaviour of compounds with ether and ester linkages is comparable, showing N* and SmA phases. The melting points of the compounds with ether linkages are in the same range as those of the ester compounds, but the liquid crystal transition temperatures are lower. The smectic layer spacings and smectic ordering properties are also similar. The cyanobiphenylyl compounds have an interdigitated SmA layer structure, which shows a small odd–even effect with spacer parity. The alkoxybiphenylyl compounds have a monolayer SmA phase for short spacers and an intercalated SmA phase for longer spacers. The selective reflection wavelengths of the chiral nematic phase of the ether compounds are lower than those of the corresponding ester compounds. The transition from N* to interdigitated or monolayer SmA is accompanied by a strong increase in the selective reflection wavelength, indicative of an intermediate TGB phase. This is absent for the transition from N* to intercalated SmA.

1. Introduction

Dimer liquid crystals form a class of mesogenic molecules in which a flexible spacer connects two mesogenic units. These compounds show several intriguing properties such as the strong odd–even effects in their physical properties observed for the phase transition temperatures and isotropization enthalpies as a function of spacer parity [1–4]. This makes these dimers interesting as model compounds for main chain liquid crystalline polymers. Another interesting phenomenon of dimer liquid crystals with smectic phases is the variation found in the smectic layer spacings [1–9].

Depending on spacer length, terminal group length and dipole moment in one or both mesogenic groups, monolayer, intercalated and interdigitated smectic phases have been found.

Dimer liquid crystals with one substituted aromatic group and one cholesteryl moiety are especially interesting because they are chiral and strongly asymmetric. The cholesteryl and aromatic 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 aromatic group. For these unsymmetrical dimers with cholesteryl moieties, three different SmA modifications were also observed, depending on spacer length, type of aromatic mesogen and length and nature of the terminal group [10–17]. The smectic layer spacings obtained by X-ray diffraction for cholesteryl dimers with alkyl terminal chains on the aromatic mesogenic groups have been investigated. They indicate that intercalated smectic phases with a d/l ratio of about 0.5 are present when the spacer is longer, and monolayer 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. 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 [16, 17]. Also, a range of twist grain boundary phases (TGB) was found. In most cases they exist over a temperature range of only a few degrees, but sometimes much larger ranges have been reported for cholesterol-containing dimers and oligomers [10–15, 18–23]. For dimers with

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long terminal groups SmC* phases were also found [10–15, 22–24].

Due to the chiral nature of the cholesteryl group, the nematic phase has a helical structure, whose pitch can be in a range where it can selectively reflect visible light of a certain wavelength. It was shown for a series of cholesteryl cyanobiphenylyloxyalkanoates that this selective reflection wavelength exhibits a strong odd–even effect as a function of spacer parity [25, 26]. This was also found for some other chiral dimers and trimers [27–33]. The influence of the connecting group between the spacer and mesogenic groups on the alternating properties of dimer liquid crystals has been the subject of investigations. It was found that the alternating properties decrease strongly upon going from methylene to ether to carbonate linking groups [4]. This was attributed to the change in bond angle in this series. Recently, a series of cholesterol-containing dimers with two ester linkages was investigated [33] and the alternation in properties was approximately similar to some series we investigated earlier, although the temperature dependence of the selective reflection wavelengths was somewhat different [25, 26].

The compounds that we have studied to date all had an ester group as the linkage between the cholesteryl group and the spacer. In this paper we describe cholesteryl dimers that contain ether linkages between the spacer and both mesogenic groups. This allows us to investigate a more complete series of homologues from commercially available spacers than with ω-substituted carboxylates as spacers. This also allows us to study the influence of the change in linking group on the liquid crystalline properties. We studied three series of compounds of which the ester derivatives showed three types of SmA modifications [16, 34, 35]. We compared their liquid crystalline properties, especially their layer spacings in the SmA phase and the selective reflection wavelength in the chiral nematic phase.

2. Experimental

2.1. *Synthesis*

Cholest-5-en-3β-tosylate [36], cholest-5-en-3β-oxyalkan-ω-ols, cholest-5-en-3β-oxyalkane-ω-tosylates, ω-bromo-1-(cholest-5-en-3β-oxy)alkanes [37, 38] and 4-alkoxy-4′-hydroxybiphenyls [39] were prepared as described in the literature.

2.1.1. *1-(Cholest-5-en-3β-oxy)-11-(4-cyanobiphenylyl-4′-oxy)undecane* ***(I-11)***

A mixture of 0.5 mmol of 11-bromocholest-5-en-3β-oxyundecane, 0.55 mmol of 4-hydroxy-4′-cyanobiphenyl and 1 g of anhydrous potassium carbonate were heated at reflux in 20 ml of butanone for 20 h. After cooling, the solvent was evaporated; 20 ml of dichloromethane was added to the residue and the salts were filtered off. The filtrate was concentrated and the product isolated by column chromatography on silica gel with dichloromethane as eluent. Recrystallization from dichloromethane/petroleum ether afforded the pure compound; yield 84 %. ^{1}H NMR: δ ($CDCl_3$) 7.65 (2d, 4H, Ar), 7.52 (d, 2H, Ar), 7.02 (d, 2H, Ar), 5.32 (m, 1H, –CH), 4.00 (t, 2H, Ar–OCH_2), 3.42 (t, 2H, –OCH_2), 3.12 (m, 1H, –OCH), 2.43–0.66 (aliphatic, 43H). Elemental analysis: found C 83.26, H 10.47, N 1.81; calc. C 83.48, H 10.37, N 1.87%.

All other dimer liquid crystals **I-*n***, **II-*n*** and **III-*n*** were prepared by the same procedure.

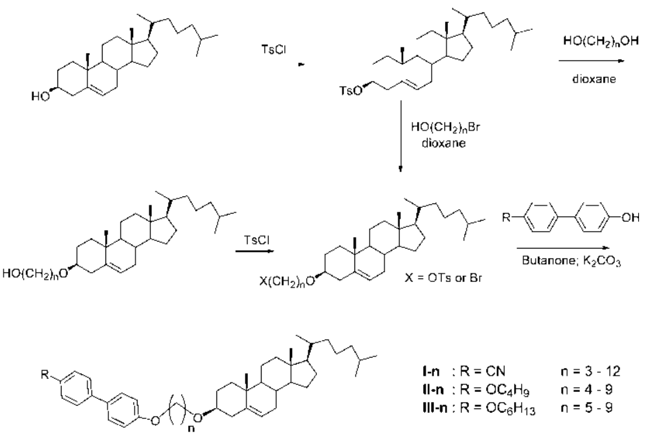
2.2. *Measurements*

Melting points, thermal phase transition temperatures and optical inspection of the liquid crystalline phases were determined on samples between ordinary glass slides using an Olympus BH-2 polarizating 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 3–7 mg samples in 30 μl sample pans and a scan rate of $10^\circ C\,min^{-1}$. 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.

Temperature-dependent X-ray curves were measured on a Philips X'pert Pro MRD machine equipped with an Anton Paar camera. 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. The selective reflection wavelengths were determined as a function of temperature by measuring the transmission spectra of the chiral nematic phases of the compounds. This was done by inserting the hot stage with a planar-oriented cholesteric sample between parallel glass slides into the measuring beam of a Hewlett Packard 8452A diode array spectrophotometer.

3. Results and discussion

The synthesis of the compounds is depicted in scheme 1. Cholest-5-en-3β-tosylate was reacted for 24 h with a six-fold excess of alkanediol or bromoalkanol in refluxing dioxane to give the cholest-5-en-3β-oxyalkan-ω-ols or the ω-bromo-1-(cholest-5-en-3β-oxy)alkanes, respectively, in 70–80% yield [37, 38]. Cholest-5-en-3β-oxyalkan-ω-ols were then converted into the tosylates [38]. Finally, reaction of the ω-bromo-1-(cholest-5-en-3β-oxy)alkanes



Scheme 1.

or the cholest-5-en-3β-oxyalkane-ω-tosylates with the appropriate hydroxybiphenyl compound in refluxing butanone with potassium carbonate as a base gave the dimer liquid crystals in good yield. The final products gave ^{1}H NMR spectra in agreement with the proposed structure, give single spots on TLC and correct C, H and N analyses. The liquid crystalline properties were determined by polarizing optical microscopy (POM), DSC and X-ray diffraction (XRD).

3.1. *1-(Cholest-5-en-3β-oxy)-ω-(4-cyanobiphenylyl-4′-oxy)alkanes **I-n***

The phase transition temperatures together with the reduced transition entropies ($\Delta S/R$) are given in table 1. The transition temperatures of the cyanobiphenyl compounds are also graphically represented in figure 1 and the entropy changes expressed as $\Delta S/R$ at the liquid crystalline transitions in figure 2. In both figures the properties of the corresponding ester derivatives **IV-*n*** (scheme 2) are also plotted. In order to make a correct comparison, ethers and esters with the same number of flexible units in the spacers have to be compared. The number of flexible units m in the spacer is $n+2$ for ethers and $n+3$ for esters.The compounds exhibit a chiral nematic (N*) phase and a smectic A (SmA) phase, which for some compounds is monotropic.

Table 1. Phase transition temperatures (°C), reduced entropy changes $\Delta S/R$ of the liquid crystalline transitions (in square brackets), smectic layer spacings d (Å) and d/l values of 1-(cholest-5-en-3β-oxy)-ω-(4-cyanobiphenylyl-4′-oxy)alkanes **I-*n***.

Compound	M. p.	SmA–N*		N*–I		*d*	*d*/*l*
I-3	139[a]	(110)	[0.37]	(118)	[0.17]	[b]	[b]
I-4	151	178	[0.12]	210	[1.06]	56.5	1.57
I-5	111	119	[0.26]	146	[0.34]	57.3	1.57
I-6	105[a]	150	[0.17]	188	[1.09]	61.4	1.62
I-7	119	(106)	[0.22]	147	[0.39]	62.8	1.63
I-8	130	(129)	[0.16]	172	[0.97]	64.8	1.62
I-9	89	97	[0.32]	144	[0.59]	65.6	1.62
I-10	109	115	[0.27]	160	[1.20]	68.9	1.64
I-11	86	89	[0.27]	140	[0.60]	71.2	1.68
I-12	106	(105)	[0.23]	151	[1.17]	77.0	1.75

[a] Another low melting modification was found at 114°C for **I-3** and at 89°C for **I-6**.

[b] Not determined.

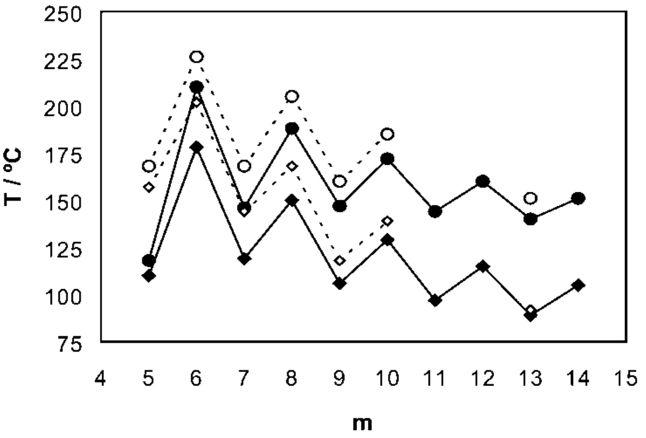


Figure 1. SmA–N* (diamonds) and N*–I (circles) phase transition temperatures of the ether compounds **I-*n*** (solid lines; closed symbols) and the ester compounds **IV-*n*** (dotted lines; open symbols) versus m, which is $n+2$ for **I-*n*** and $n+3$ for **IV-*n***.

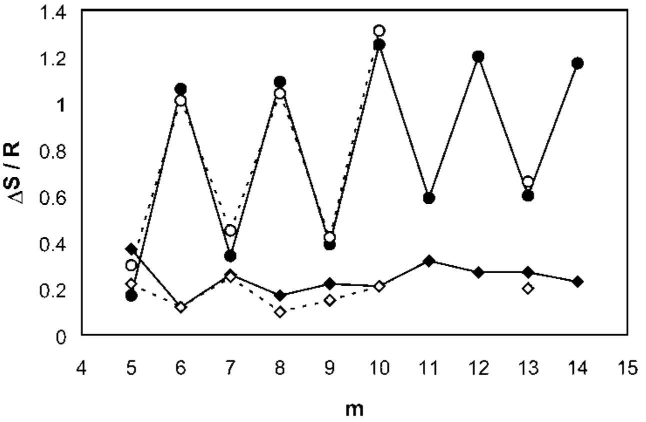
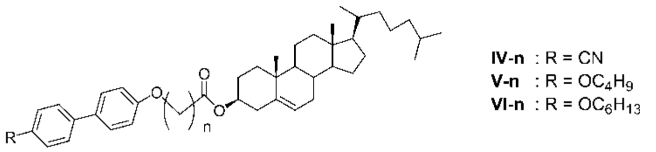


Figure 2. Reduced entropy changes $\Delta S/R$ of the SmA–N* (diamonds) and N*–I (circles) phase transitions of the ether compounds **I-*n*** (solid lines; closed symbols) and the ester compounds **IV-*n*** (dotted lines; open symbols) versus m, which is $n+2$ for **I-*n*** and $n+3$ for **IV-*n***.



Scheme 2.

The transitions from SmA to N* are accompanied by a TGB phase which is a few degrees wide. This is indicated by the growth of spiral lines in a planar-oriented SmA phase upon heating under a polarizing microscope, and a sharp increase in the selective reflection wavelength upon cooling from the N* phase. With DSC no separate peaks are found for the N*–TGB and TGB–SmA transitions and the enthalpy changes are calculated from the total broadened peak.

The liquid crystalline properties of this series of compounds are similar to those of the corresponding ester derivatives **IV-*n*** [25, 26]. A pronounced odd–even effect is seen in the N–I (isotropic) and the SmA–N to transitions, which attenuates with increasing spacer length. The melting points are in the same range as those of the ester compounds, but the liquid crystalline transitions are about 10 to 30°C lower, especially for shorter spacers. The ester groups seem to stabilize the liquid crystalline phase more than the ether groups, probably through a stronger mutual interaction through their dipoles. A strong odd–even effect is also observed for the $\Delta S/R$ values of the isotropization transition. For the SmA–N* transition there seems to be a much smaller reversed odd–even effect. This could mean that the difference in ordering between the odd and even members in the SmA phase is smaller than in the N* phase. A similar effect was found for the ester compounds **IV-*n*** [25, 26]. It was found that for symmetric dimers with different linkages between the mesogenic units the odd–even effects strongly decrease upon going from methylene to ether to carbonate [4, 40]. Such a difference in odd–even effect is absent in our compounds upon going from ester to ether; apparently, the accompanying change in overall geometry is small.

The selective reflection wavelength (λ_{sel}) of this series of compounds was measured as a function of temperature, except for the compound **I-3**, because for this compound the whole smectic range was monotropic. As can be seen in figure 3, the λ_{sel} of the compounds with an even spacer are larger than for those with an odd spacer. For the present compounds λ_{sel} is almost temperature independent in a large part of the N* range. Only near the transition to the smectic phase does λ_{sel} increase sharply. In fact this indicates the transition to a TGB phase, which is present for a few degrees between the N* and the SmA phases. The presence of the TGB phase is also indicated by the sudden growth of spiral lines upon heating a homeotropically aligned SmA film under POM. For the compounds with an even spacer λ_{sel} decreases slightly with n. For the compounds with an odd spacer λ_{sel} seems to increase slightly with n, although the precise determination of λ_{sel} by the method used was hampered by the absorption of light by the glass slides and also by absorption by the aromatic group of the compounds.

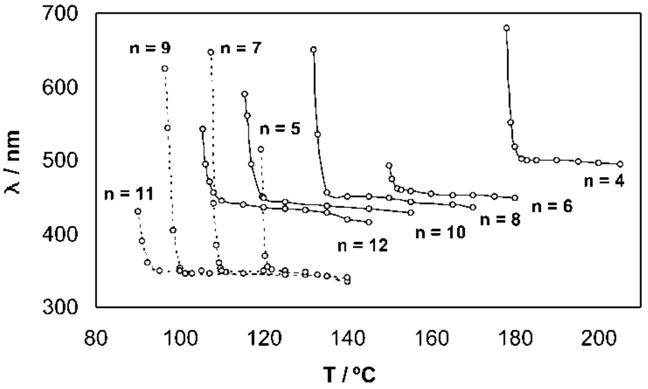


Figure 3. Selective reflection wavelengths λ_{sel} (nm) of the chiral nematic phases of compounds **I-*n*** plotted as a function of temperature. Even compounds are represented by solid lines and odd compounds by dotted lines.

The results for these compounds differ somewhat from those found for the corresponding ester compounds **IV-*n*** [25, 26]. A similar odd–even effect was seen, but the selective reflection wavelengths were significantly larger and in particular, the temperature dependence of the compounds with an even spacer was much larger, giving larger λ_{sel} values with decreasing temperature. The difference between the two series of compounds could be related to the presence of the carbonyl group in the ester series. This group could enhance the parallel alignment of the molecules in the N* phase due to the additional dipole, and thus decrease the helical twisting power, resulting in larger λ_{sel} values for the ester compounds. Upon decreasing the temperature this influence becomes stronger, which could explain the temperature dependence of the ester-containing dimers with an even spacer. Because the ether compounds lack such a carbonyl group the λ_{sel} values are lower and the temperature dependence is less. In a recent paper on cholesteryl dimers with two ester linkages in the spacer, the temperature dependence of the λ_{sel} was stronger than in both the ether compounds **I-*n*** and the ester compounds **IV-*n*** [33]. This could mean that the difference in geometry between the ester and ether compounds is probably less important. The difference between the selective reflection wavelengths of the odd and even chiral dimers and the effect of temperature on the cholesteric pitch of chiral dimers has been attributed to the formation of smectic clusters in the cholesteric phase [33] or differences in the elastic constants [31].

Previously, we presented X-ray results that indicated that the smectic phases of the cyanobiphenylyl-containing dimers with an ester spacer were interdigitated [16]. The

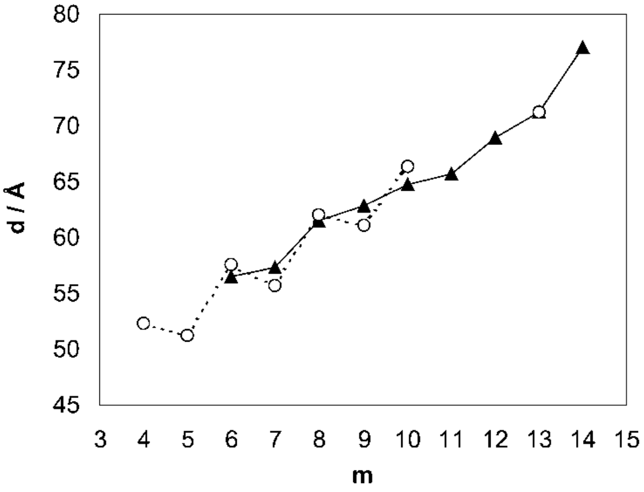


Figure 4. Comparison of the smectic layer spacings d (Å) of compounds **I-*n*** (–▲–) and the corresponding ester compounds **IV-*n*** (–○–) plotted versus m, which is $n+2$ for the ether compounds **I-n** and $n+3$ for the ester compounds **IV-*n***.

results of XRD measurements for the smectic phases of both the ester and ether dimers are given in figure 4, in which the smectic layer thickness d is plotted versus m. In order to compare the results of the ester and ether series, m is the number of flexible units between the mesogenic groups in the dimers. Therefore for the ether series $m=n+2$ and for the ester series $m=n+3$. The d-spacings were determined at several temperatures in the smectic phase and were found to be only weakly temperature-dependent (the d-spacings decrease slightly with temperature; the d-spacings given are from the middle of the smectic range). It is clearly seen that the d-spacings are very similar for the two series. A small odd–even effect is seen in the d-spacings: as expected those for compounds with an odd spacer are smaller than those for compounds with an even spacer. The odd–even effect is more pronounced for the ester compounds than for the ether compounds. This difference could be related to the different geometrical shapes around ester and ether groups. Although one could expect that such a difference should also be reflected in the magnitude of the odd–even effect in the transition temperatures and associated entropy changes [4, 40], this was not found.

In table 1 the layer spacing d of compounds **I-*n*** is also given, together with a value of d/l, in which l is the length of the molecule, calculated for its most extended conformation. The layer spacing is greater than the length of the molecule, indicating that the ordering in the smectic phase is interdigitated. It is remarkable that the d/l value increases with spacer length. An ordering in which the polar cyanobiphenylyl parts of the molecules compensate their dipoles by an antiparallel arrangement would give an interdigitated ordering, in which the d/l ratio increases with spacer length. Models indicate that the observed layer spacing can be obtained when the cyanobiphenylyl groups are in an antiparallel arrangement and the spacers and the cholesteryl groups are on the outside (figure 5). The cholesteryl groups have a cross sectional area about twice that of an alkyl group or an aromatic group. In the middle of the layer the aromatic groups are present; thus the alkyl spacers will not completely fill the remaining volume of space. With increasing spacer length this will destabilize the smectic phase. This agrees well with the observed increase in nematic temperature range with spacer length (figure 1).

3.2. *1-(Cholest-5-en-3β-oxy)-ω-(4-butoxybiphenylyl-4′-oxy)alkanes **II-n** and 1-(cholest-5-en-3β-oxy)-ω-(4-hexyloxybiphenylyl-4′-oxy)alkanes **III-n***

The transition temperatures of the compounds with a butoxy (**II-*n***) and hexyloxy (**III-*n***) terminal group, together with the associated entropy changes at the liquid crystalline transitions expressed as **ΔS/R** are given in table 2. Most compounds exhibit a chiral nematic and a SmA phase. The N*–I transitions show the expected odd–even effect with spacer parity and also the SmA–N* transitions as far as can be deduced from the limited number of compounds. The melting points are in the same range as those of the corresponding ester compounds [16, 34, 35], but the liquid

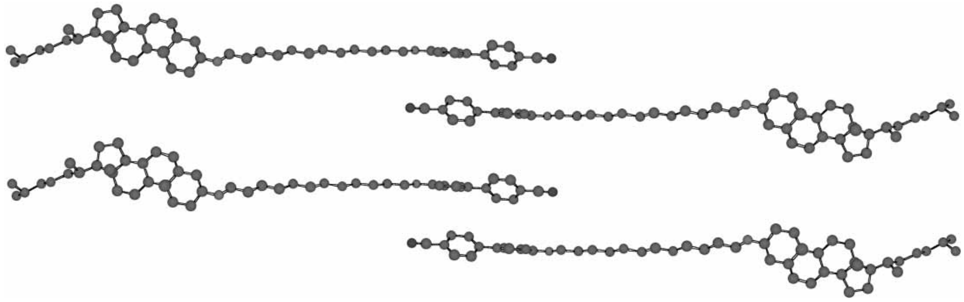


Figure 5. Model of the possible ordering in the interdigitated smectic phase of compound **I-12**.

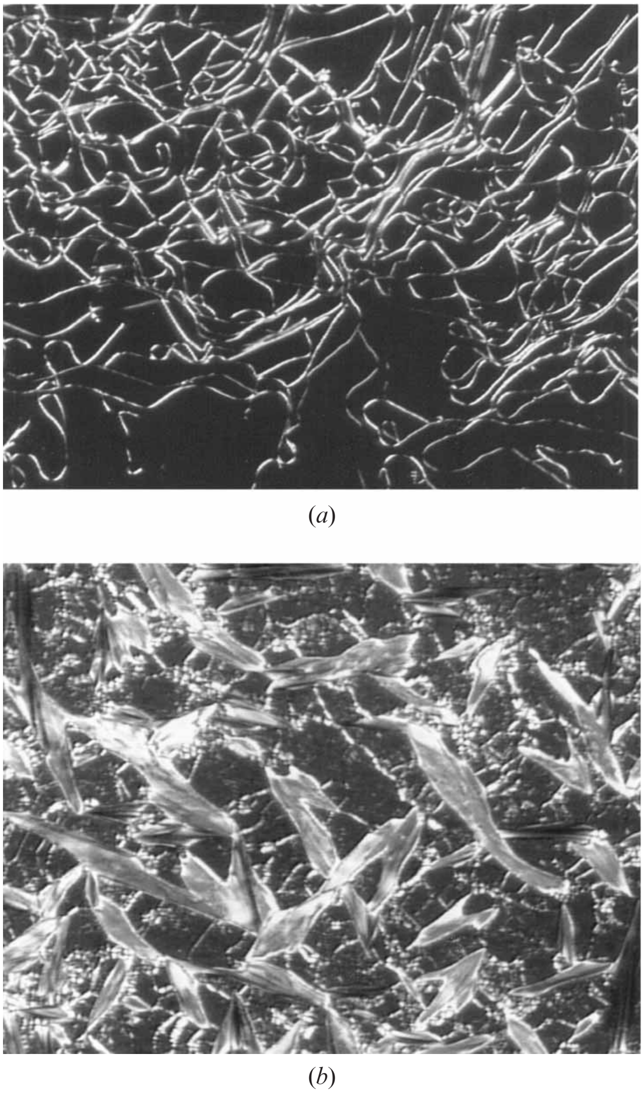
Table 2. Phase transition temperatures (°C), reduced entropy changes $\Delta S/R$ of the liquid crystalline transitions (in square brackets), smectic layer spacings d (Å) and d/l values of 1-(cholest-5-en-3β-oxy)-ω-(4-butoxybiphenylyl-4′-oxy)alkanes **II-*n*** and 1-(cholest-5-en-3β-oxy)-ω-(4-hexyloxybiphenylyl-4′-oxy)alkanes **III-*n***.

Compound	M. p.	SmA–N*		N*–I		d	d/l
II-4	160	—		189	[0.68]	—	—
II-5	119	—		133	[0.27]	—	—
II-6	128	148	[0.37]	175	[1.15]	19.0	0.46
II-7	92[a]	—		135	[0.32]	—	—
II-8	120	158	[0.60]	167	[1.43]	20.0	0.46
II-9	111	116	[0.23]	139	[0.53]	20.1	0.46
III-5	113[a]	(106)	[0.06]	131	[0.27]	41.2	0.98
III-6	143	151	[0.23]	174	[1.17]	42.3	0.96
III-7	109[a]	—		131	[0.31]	—	—
III-8	122	155	[0.82]	161	[1.45]	20.9	0.45
III-9	99	117	[0.36]	135	[0.46]	21.1	0.45

[a] Another low melting modification was found at 79°C for **II-7**, at 109°C for **III-5** and at 93°C for **III-7**.

crystalline transitions are usually at somewhat lower temperatures.

It is remarkable that the compounds with a heptamethylene spacer **II-7** and **III-7** do not show a SmA phase even though the compound can be supercooled considerably. A similar effect was observed for the corresponding ester compounds **V-6** and **VI-6** [16]. When looking at the hexyloxy compounds, those with a shorter spacer, **III-5** and **III-6**, have a smectic layer spacing that is almost equal to the molecular length, whereas those with a longer spacer, **III-8** and **III-9**, exhibit an intercalated SmA phase with a d/l ratio close to 0.5. This means that a change in smectic ordering occurs around a spacer length of seven methylene groups. Luckhurst *et al.* have found that, in a series where an ordering change occurred from interdigitated to intercalated, some compounds near such a transition were not smectic at all and showed only nematic behaviour [7]. Achard *et al.* have found that some cholesteryl-containing dimeric compounds with a spacer length about equal to the terminal chain length showed a range of incommensurate phases [10–15]. In the butoxy series, however, the transition from intercalated to monolayer smectic has not yet occurred for **II-6**, as can be seen from the d-spacing of 19.0 Å. For compound **II-5** no smectic behaviour was found.


(*a*)

(*b*)

Figure 6. Polarizing microscopy textures of (*a*) **III-6** and (*b*) **III-8** at the SmA–N* transition.

For the compounds that have a monolayer ordering in the smectic phase a TGB phase is present at the SmA to N* transitions. Upon heating a planar-oriented SmA phase of compound **III-6** under a polarizing microscope spiral lines develop, figure 6 (*a*), and a sharp increase is found in λ_{sel} upon cooling the N* phase of this compound. For **III-8**, which has an intercalated SmA phase, no intermediate TGB phase is found, as can be seen from figure 6 (*b*), where at the SmA–N* transition smectic fans growing within the blue N* phase can be observed. The fact that no TGB phase develops in chiral dimers with an intercalated SmA phase was also observed by Blatch *et al.*, who suggested that the nature of the intercalated SmA phase might well inhibit the layers from twisting into a helix [31]. This seems a plausible explanation that also fits well with our results and those of Yelamaggad *et al.* [35]. Faye *et al.* [41] however, reported a TGB phase at the intercalated SmA–N* transition in a chiral dimer compound without a cholesteryl group, so other effects may also play a role.

The selective reflection wavelengths (λ_{sel}) of the chiral nematic phase of the dimers **III-*n*** and **VI-*n*** are given as a function of temperature in figure 7. For the compounds with an odd number of flexible groups in the

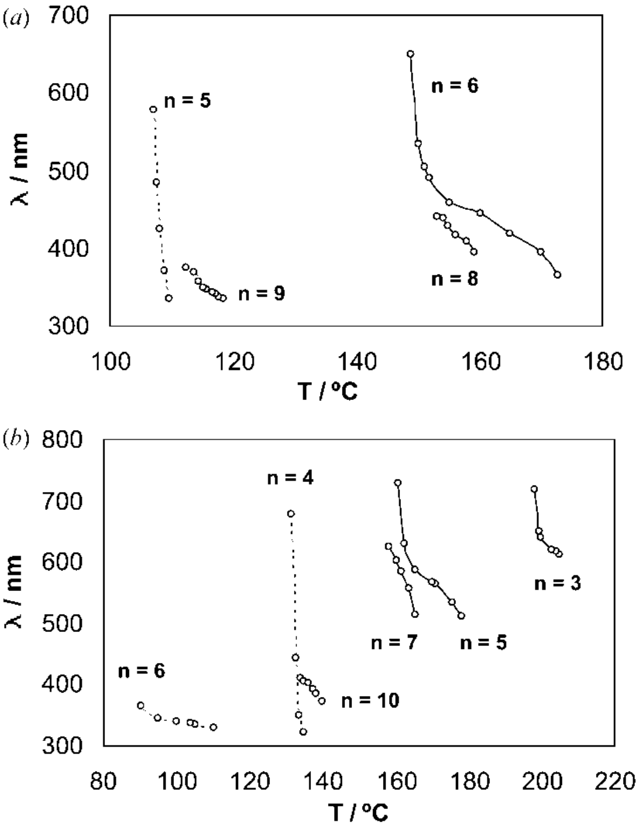


Figure 7. Selective reflection wavelengths λ_{sel} (nm) of the chiral nematic phases of compounds **III-*n*** (*a*) and the corresponding ester compounds **VI-*n*** (*b*) plotted as a function of temperature.

spacer the λ_{sel} could not always be measured, or not over the complete temperature range, because it was sometimes lower than about 330 nm. For the ester compounds only a small part of the curve was obtained for **VI-4** and **VI-6**, and for the ether compounds **III-5** and **III-9**. For this series the λ_{sel} for **III-7** could not be measured, probably because it was entirely below 330 nm. From the graphs it can be seen that the compounds with an even spacer have a λ_{sel} that is higher than for those with an odd spacer. The odd–even effect appears to decrease with spacer length, which means that for longer spacers the λ_{sel} values of the compounds with odd and even spacers become closer. These trends agree well with previous results for other series of compounds [25, 26, 28, 30–33].

Some other interesting phenomena can be seen from these graphs. When there is a transition from N* to monolayer SmA, λ_{sel} increases very strongly close to this transition, indicative of an intermediate TGB phase. For the ether compounds such a strong increase is found for **III-5** and **III-6** and for the ester compounds **VI-3**, **VI-4** and **VI-5**. If the transition is from N* to intercalated SmA, there is only a small increase in λ_{sel} and the transition to SmA is abrupt. The ether compounds show lower λ_{sel} than the ester compounds; this was also observed for the cyanobiphenyl compounds. This is probably also the reason why for **III-7**, which does not have a SmA phase, the λ_{sel} could not be measured, because it is below 330 nm.

The butoxy compounds **II-*n*** show a similar behaviour. For both the ether and ester compounds with butoxy tails the λ_{sel} values are slightly higher than for the hexyloxy compounds. For the compounds with an odd spacer λ_{sel} could also not be measured for the whole temperature range. Only near the transition to the SmA phase is it observed above 330 nm. Interestingly, the ester **V-4** shows a strong increase in λ_{sel} near 100°C, which would indicate a transition to a TGB phase and thus to a monolayer SmA phase. This SmA phase is however not observed by DSC or POM, due to crystallization near this temperature. For the corresponding ether compound **II-5** such an increase in λ_{sel} upon cooling is not observed, probably because this compound crystallizes before the transition to TGB (or SmA) is reached.

Thus it seems that both ether and ester cholesteryl- and alkoxybiphenylyl-containing dimers can have a monolayer and an intercalated SmA structure. The behaviour of the ester and ether compounds is quite similar. Which phase is formed depends partly on the length of the terminal alkyl tail in relation to the spacer length, and also on the parity of the spacer. For odd spacers, the smectic phase is destabilized near the transition from monolayer to intercalated structure and consequently no SmA phase was found for the compounds **II-7**, **III-7**, **V-6** and **VI-6**, even though these compounds can be supercooled considerably. For even spacers a smectic phase is always observed. The dependence on terminal alkyl chain length is, for example, clearly seen in the different smectic ordering between compounds **II-6** and **III-6** and also between **V-5** and **VI-5**, which are monolayer for a hexyloxy terminal group and intercalated for a butyloxy terminal group. For a similar series of ether compounds with the much longer dodecyloxy terminal group we observed only monolayer smectic phases up to decamethylene spacers [24].

4. Conclusions

The properties of three series of cholesterol containing dimer liquid crystals with ether connections to the spacers were investigated and compared with those of the corresponding ester compounds. The phase behaviours of the ether and ester compounds are very similar, showing odd–even effects for the phase transition temperatures, isotropization entropies and selective reflection wavelengths. The compounds with ether linkages show N* and SmA phases whose transition temperatures occur at lower temperatures than those of the ester compounds. Also the selective reflection wavelengths of the N* phases are lower for the ether compounds. The SmA phases of the cyanobiphenylyl compounds are interdigitated ($d/l > 1.5$) and show a small odd–even effect that is more pronounced for the ester compounds. Both the ether and ester series of the alkoxybiphenylyl compounds have monolayer SmA phases for short spacers ($d/l \sim 1.0$) or intercalated SmA phases for longer spacers ($d/l \sim 0.5$). The transition between these different orderings depends on the length of the alkoxy tail and of the spacer. For compounds with an odd spacer, one compound in the series near this transition shows no smectic behaviour at all. The selective reflection wavelengths of the N* phases of the compounds with a butoxy tail are slightly higher than those of the corresponding compounds with a hexyloxy tail.

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