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Odd-even effects in the thermotropic and optical properties of three series of chiral twin liquid crystals

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Three series of novel chiral twin liquid crystals consisting of a cholesteryl and a 4'-cyanobiphenyl-4-yloxy group (III) or a 4-cyanophenoxy group (IV) and of a dihydrocholesteryl and a 4'-cyanobiphenyl-4-yloxy group (V) connected by an alkanate spacer with a varying number (1-7 and 10) of methylene units were synthesized and their mesogenic properties investigated. Strong odd-even effects were observed as a function of spacer length for the phase transition temperatures, the corresponding entropy changes and the selective reflection wavelengths associated with the chiral nematic phase. The compounds with an even number of methylene units have a smaller pitch than the compounds with an odd number of methylene units. Replacement of the cholesteryl group by a dihydrocholesteryl group results in an larger pitch, whereas replacement of the 4'-cyanobiphenyl-4-yloxy group by a 4-cyanophenoxy group gives a smaller pitch.

1. Introduction

Twin liquid crystalline compounds consisting of two mesogenic parts connected by a flexible spacer constitute an interesting class of liquid crystal materials. Although the first examples of these compounds were described more than sixty years ago [1], they have recently gained renewed attention, stimulated by the realization that they can be considered as models for main chain [2, 3] and also side chain liquid crystalline polymers [4, 5].

One of the most interesting features of twin liquid crystals is that the physical properties associated with the nematic phase alternate with the number of flexible units in their spacer [6-11]. This odd-even effect has been explained by the different ordering of the mesogens in the nematic phase depending on the number of flexible units in the spacer [12-14]. The better ordered nematic phase is obtained with an even number of flexible units in the spacer, leading to a higher nematic-isotropic phase transition temperature and a higher associated entropy change.

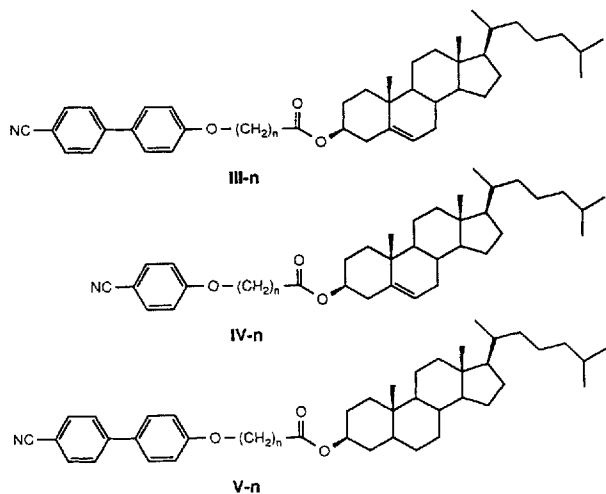
Most of the twin liquid crystals that have been investigated so far contain two identical mesogenic units, but some compounds with two different aromatic mesogenic units have recently been investigated by Luckhurst *et al.* and have been shown to exhibit interesting S_A phases [15]. Only a few chiral twin liquid crystalline compounds have been reported in literature. Some cholesteryl ω -aryl-

carboxylates have been investigated and their thermotropic properties have been shown to exhibit an odd-even effect with spacer length [16-21]. However, no systematic investigation of the optical properties has been performed. Since the pitch of the helical conformation of a chiral nematic phase is also influenced by the ordering of the molecules in this phase [22-24], an odd-even effect in the selective reflection wavelengths of chiral nematic twin liquid crystals may be anticipated. It has been observed that a chiral centre in the alkyl chain of liquid crystalline compounds has a pronounced effect on the pitch of the nematic phase and the helix sense has been found to alternate with the number of flexible units between the aromatic core and the chiral centre where the flexible unit can be a methylene, an ether or a carbonyl group [25-29]. Compounds of this type have usually been investigated as a dilute solution in a nematic solvent and the helical twisting power of these compounds also depends on the interaction of the chiral compounds with the solvent. It has for example been found that the helical twisting power of a chiral compound in a nematic shows an odd-even effect as a function of alkyl spacer length of the solvent [22-24, 30]. Recently chiral twin liquid crystals have been studied in which the chirality stems from a chiral centre in the spacer [31, 32] and also some cholesteryl esters of dicarboxylic acids have been reported [33]. In a recent communication we have shown that both the thermotropic and optical properties of a series of cholesteryl ω -(4'-cyanobiphenyl-4-yloxy)alkanoates

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have a pronounced odd–even effect with spacer length [34].

In this paper, a more detailed study is described concerning the odd–even effects in the optical and thermotropic properties of three series of related chiral twin liquid crystals; the study is also directed at determining the influence of different mesogenic structures on these properties.



2. Experimental

2.1. Synthesis

2.1.1. General method for the synthesis of the cholesteryl and dihydrocholesteryl ω -bromoalkanoates **I-3-I-10** and **II-3-II-10** and the chloroacetyl derivatives **I-1** and **II-1**

These compounds were prepared according to literature methods [35,36]. The appropriate ω -bromocarboxylic acid (10 mmol) was converted into the acid chloride by refluxing in thionyl chloride for 0.5 h. After evaporation of the unreacted thionyl chloride, the ω -bromocarboxylic acid chloride or the commercially available chloroacetyl chloride was dissolved in 5 ml of benzene and this solution was added over a period of 0.25 h to a solution of cholesterol or dihydrocholesterol (12 mmol) and triethylamine (25 mmol) in 10 ml of benzene at 5°C. After stirring at 5°C for 0.5 h, the mixture was left for 16 h at room temperature. The mixture was washed with 1 M HCl, dried over magnesium sulphate and concentrated. The products were purified by recrystallization from acetone. Yields 60–70 per cent **I-7**: $^1\text{H NMR}$ (CDCl_3) δ 5.4 (d, 1 H, C=CH), 4.6 (m, 1 H, CHO), 3.4 (t, 2 H, CH_2Br), 2.3 (t, 2 H, $\text{CH}_2\text{C}=\text{O}$), 2.1–0.8 (m, 53 H, aliphatic). Elemental analysis, calculated ($\text{C}_{35}\text{H}_{59}\text{BrO}_2$): C, 71.04; H, 10.05; found C, 70.81; H, 10.09 per cent.

2.1.2. 3-(4-Cyanophenoxy)propanoic acid and 3-(4'-cyanobiphenyl-4-yloxy)propanoic acid

A solution of 20 mmol of sodium ethanoate in 20 ml of ethanol was added to a solution of 10 mmol of 4-(4-cyanophenyl)phenol or 4-cyanophenol and 10 mmol of 3-bromopropanoic acid in 15 ml of ethanol. The mixture was boiled for 16 h and subsequently concentrated. The residue was treated with 25 ml of 1 M HCl and shaken with ethyl acetate. The organic layers were dried with magnesium sulphate and concentrated. The residue was triturated with ether, filtered and washed with cold ether to give 3-(4'-cyanobiphenyl-4-yloxy)propanoic acid (m.p. 168°C; yield 10 per cent; $^1\text{H NMR}$ (CDCl_3) δ 7.8–7.0 (m, 8 H, aromatic), 4.3 (t, 2 H, CH_2O), 2.8 (t, 2 H, $\text{CH}_2\text{C}=\text{O}$); Elemental analysis calculated ($\text{C}_{16}\text{H}_{13}\text{NO}_3$): C, 71.90; H, 4.90; N, 5.24; found: C, 71.72; H, 4.84; N, 5.03 per cent) or 3-(4-cyanophenoxy)propanoic acid (m.p. 143°C; yield 15 per cent; $^1\text{H NMR}$ (CDCl_3) δ 7.6 (m, 2 H, aromatic), 6.9 (m, 2 H, aromatic), 4.2 (t, 2 H, CH_2O), 2.7 (t, 2 H, $\text{CH}_2\text{C}=\text{O}$); Elemental analysis calculated ($\text{C}_{10}\text{H}_9\text{NO}_3$): C, 62.82; H, 4.74; N, 7.33; found: C, 62.62; H, 4.72; N, 7.12 per cent).

2.1.3. General method for the synthesis of **III-2**, **IV-2** and **V-2**

A solution of 1 mmol of 3-(4'-cyanobiphenyl-4-yloxy)propanoic acid or 3-(4-cyanophenoxy)propanoic acid in thionyl chloride was boiled for 0.5 h. The excess of thionyl chloride was removed under reduced pressure and the residue was dissolved in 5 ml of benzene. This solution was added to a solution of 1 mmol of cholesterol or dihydrocholesterol and 1 mmol of triethylamine in 10 ml of benzene at 5°C. After 1 h at 5°C and 16 h at room temperature, the reaction mixture was concentrated and the residue was purified by column chromatography on silica gel using petroleum ether b.p. 40–60°/dichloromethane (1:1) as eluent and recrystallization from petroleum ether b.p. 60–80. Yields 35 per cent **III-2**: $^1\text{H NMR}$ (CDCl_3) δ 7.8–6.9 (m, 8 H, aromatic), 5.4 (d, 1 H, C=CH), 4.7 (m, 1 H, CHO), 4.3 (t, 2 H, CH_2O), 2.8 (t, 2 H, $\text{CH}_2\text{C}=\text{O}$), 2.3–0.7 (m, 43 H, aliphatic). Elemental analysis calculated ($\text{C}_{43}\text{H}_{57}\text{NO}_3$): C, 81.21; H, 9.04; N, 2.20; found: C, 80.98; H, 8.93; N, 2.19 per cent.

2.1.4. General method for the synthesis of the other compounds of series **III**, **IV** and **V**

A mixture of 1 mmol of 4-(4-cyanophenyl)phenol or 4-cyanophenol, 1.1 mmol of the appropriate cholesteryl or dihydrocholesteryl ω -bromo- or ω -chloro-alkanoate (**I** or **II**) and 1 g of anhydrous potassium carbonate in 20 ml of butanone was heated under reflux for 16 h. The solvent was evaporated and the residue was 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 was purified by column chromatography on silica gel with petroleum ether b.p. 40–60° dichloromethane (1 : 1) as eluent and recrystallization from petroleum ether b.p. 60–80°. Yields 80–90 per cent. **V-10**: $^1\text{H NMR}$ (CDCl_3) δ 7.8–6.9 (m, 8 H, aromatic), 4.7 (m, 1 H, CHO), 4.0 (t, 2 H, CH_2O), 2.3 (t, 2 H, $\text{CH}_2\text{C}=\text{O}$), 2.0–0.7 (m, 62 H, aliphatic). Elemental analysis calculated ($\text{C}_{51}\text{H}_{75}\text{NO}_3$): C, 81.66; H, 10.08; N, 1.87; found: C, 81.88; H, 10.14; N, 1.91 per cent.

2.2. Measurements

Melting points and thermal phase transition temperature determination and optical inspection of the liquid crystalline phases were carried out on samples mounted between glass slides, using an Olympus BH-2 polarizing microscope equipped with a Mettler FP82HT hot stage, which was 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 a sample between parallel glass slides in the measuring beam of a Hewlett Packard 8452A diode array spectrophotometer or a Cary 5E UV/VIS/NIR spectrophotometer. Differential scanning calorimetry (DSC) thermograms were obtained using 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.

3. Results and discussion

Most of the compounds of these series are conveniently prepared in high yield by coupling of 4-(4-cyanophenyl)phenol or 4-cyanophenol with the appropriate cholesteryl or dihydrocholesteryl ω -bromoalkanoate in butanone with potassium carbonate as base. This route was not applicable to the synthesis of the twins with $n = 2$, because attempts to prepare **I-2** or **II-2** by coupling of 3-bromopropanoic acid with cholesterol or dihydrocholesterol gave acrylates due to elimination of HBr under the reaction conditions. However, twins with $n = 2$ could be obtained by first preparing 3-(4'-cyanobiphenyl-4-yloxy)propanoic acid or 3-(4-cyanophenyl)propanoic acid followed by coupling with cholesterol or dihydrocholesterol. For this route only low yields were obtained. The structure and purity of the new compounds were proven by $^1\text{H NMR}$ spectroscopy, single spot behaviour on thin layer chromatograms and correct C, H and N elemental analyses.

Observation of the liquid crystalline phases under the polarizing microscope showed that the cholesteric phase is easily aligned in a planar orientation between ordinary untreated glass slides. Upon applying mechanical stress to the S_A phases, usually a highly aligned homeotropic phase was obtained.

Table 1. Melting points (m.p.) and monotropic chiral nematic–isotropic ($\text{N}^* \rightarrow \text{I}$) phase transition temperatures ($^\circ\text{C}$) of cholesteryl and dihydrocholesteryl ω -bromoalkanoates **I-3-I-10** and **II-3-II-10** and the cholesteryl and dihydrocholesteryl chloroacetates **I-1** and **II-1**.

Compound	m.p.	$\text{N}^* \rightarrow \text{I}$	Compound	m.p.	$\text{N}^* \rightarrow \text{I}$
I-1	163	†	II-1	149	†
I-3	87	90	II-3	76	†
I-4	100	(90)	II-4	71	(52)
I-5	121	(84)	II-5	74	†
I-6	110	(77)	II-6	79	(57)
I-7	85	(80)	II-7	74	†
I-10	100	(76)	II-10	67	(55)

† Not observed.

Parentheses indicate a monotropic transition.

The melting points of the cholesteryl and dihydrocholesteryl ω -haloalkanoates are given in table 1. For several of these compounds, a monotropic chiral nematic liquid crystalline phase could be observed. The melting points and the chiral nematic–isotropic ($\text{N}^* \rightarrow \text{I}$) transition temperatures of the cholesteryl compounds are somewhat higher than those for the dihydrocholesteryl compounds.

The melting points and the chiral nematic–isotropic and smectic A–chiral nematic ($S_A \rightarrow \text{N}^*$) phase transition data of compounds **III**, **IV** and **V** are given in table 2. For compounds **III-1**, **IV-1** and **V-1**, a nematic phase could not be observed and the S_A phase transforms directly into the isotropic phase upon heating. In figures 1, 2 and 3, the melting points and liquid crystalline phase transition temperatures are plotted versus n , the number of methylene units in the flexible alkanate spacer.

Figure 1 clearly shows that all $\text{N}^* \rightarrow \text{I}$ and $S_A \rightarrow \text{N}^*$ transitions of the cholesteryl cyanobiphenyloxy compounds **III** occur above the melting point and therefore are enantiotropic, except the $S_A \rightarrow \text{N}^*$ transition of **III-10** which lies only a few degrees below the melting point. Previously investigated cholesteryl ω -arylalkanoates mainly show monotropic liquid crystalline behaviour [17–21]. For compounds **IV** all $S_A \rightarrow \text{N}^*$ transitions and the $\text{N}^* \rightarrow \text{I}$ transitions of the compounds with an even number of methylene groups in their spacers are monotropic (see figure 2) and only the $\text{N}^* \rightarrow \text{I}$ transitions of **IV-3**, **IV-5** and **IV-7** are enantiotropic. For compounds **V**, most of the $S_A \rightarrow \text{N}^*$ and $\text{N}^* \rightarrow \text{I}$ transitions are enantiotropic (see figure 3). This indicates that the 4'-cyanobiphenyl-4-yloxy group has a more positive effect on the occurrence of thermodynamically stable liquid crystalline phases than the cyanophenoxy group. The same is observed for the cholesteryl group as compared to the dihydrocholesteryl group.

It is interesting to note that the chiral nematic temperature range increases with increasing spacer length. For most liquid crystalline compounds this range

Table 2. Melting points (m.p.), smectic A–chiral nematic ($S_A \rightarrow N^*$) and chiral nematic–isotropic ($N^* \rightarrow I$) phase transition temperatures ($^{\circ}\text{C}$) of compounds **III-*n***, **IV-*n*** and **V-*n***. The corresponding entropy changes $\Delta S/R$ in square brackets.

Compound	m.p.		$S_A \rightarrow N^*$		$N^* \rightarrow I$	
III-1	176	[7.7]	210‡ (2.07)‡			
III-2	152	[8.4]	157	[0.22]	168	[0.30]
III-3	160	[7.2]	202	[0.12]	226	[1.01]
III-4	118†	[7.8]	144	[0.25]	168	[0.45]
III-5	128†	[5.9]	168	[0.10]	205	[1.04]
III-6	103	[12.5]	118	[0.15]	160	[0.42]
III-7	127	[11.9]	139	[0.21]	185	[1.31]
III-10	97	[8.5]	(92)	[0.20]	151	[0.66]
IV-1	135	[8.8]	128‡ [2.28]‡			
IV-2	131	[7.7]	(95)	[0.34]	(104)	[0.25]
IV-3	135	[11.9]	(128)	[0.62]	140	[0.57]
IV-4	122	[12.0]	(82)	[0.36]	(101)	[0.31]
IV-5	120†	[10.1]	(102)	[0.38]	131	[0.54]
IV-6	100	[10.7]	(65)	[0.33]	(90)	[0.35]
IV-7	93	[9.9]	(76)	[0.43]	119	[0.81]
IV-10	99	[16.5]	§		(94)	[0.44]
V-1	188	[10.8]	195‡ [2.07]‡			
V-2	170	[15.4]	(151)	[0.42]	(159)	[0.42]
V-3	171	[10.0]	192	[0.10]	209	[1.01]
V-4	139	[10.6]	140	[0.21]	156	[0.39]
V-5	134	[10.5]	162	[0.17]	190	[1.11]
V-6	137	[12.4]	(116)	[0.17]	146	[0.49]
V-7	127	[10.9]	137	[0.13]	172	[1.27]
V-10	104	[14.0]	(91)	[0.31]	137	[0.79]

† These compounds may exist in another crystalline form with a lower melting point: **III-4**: 101 $^{\circ}\text{C}$; **III-5**: 90 $^{\circ}\text{C}$; **IV-5**: 105 $^{\circ}\text{C}$.

‡ These values correspond to a $S_A \rightarrow I$ transition.

§ Not observed.

Parentheses indicate a monotropic transition.

decreases with increasing alkyl chain in favour of a smectic phase [37, 38]. For some series of symmetrical dimer liquid crystals an increased nematic range was also observed upon increasing the spacer [39]. The increase of this range with spacer length does not differ much for the three series, but seems to be the largest for series **III**. Recently, it was found that some series of non-symmetrical twin liquid crystals show an increased nematic range as a function of spacer length, and that this decreases again with longer spacer lengths [15]. This is attributed to a change from an interdigitated to an intercalated S_A phase, both of which are destabilized for intermediate spacer lengths, resulting in an increased nematic phase range. For our compounds, an interdigitated structure of the S_A phase can be expected in which the more polar and polarizable cyanophenoxy or cyanobiphenyloxy groups have an alternating stacking interaction. Since the cross-section of a cholesteryl group is about twice as large as that of a phenyl group, the layers with the cholesteryl groups and the aromatic groups are well packed. The layers containing

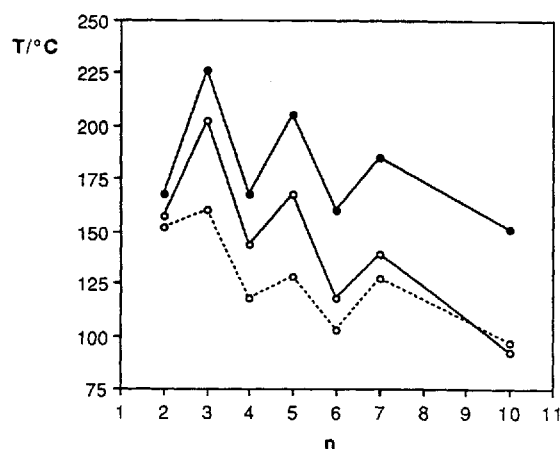


Figure 1. Dependence of the melting points (---○---), S_A-N^* (—○—) and N^*-I transition temperatures (—●—) on n , the number of methylene units in the alkanolate spacers of compounds **III-*n***.

the spacers are not as well packed due to their cross-section which is about half that of the cholesteryl groups. Therefore, we assume that with an increased spacer length a destabilization of the interdigitated S_A phase occurs, resulting in an increased nematic range with spacer length.

From figures 1, 2 and 3, it is apparent that both the S_A-N^* and N^*-I phase transition temperatures show a pronounced odd–even effect for all series. This phenomenon is well known for the N^*-I transition temperatures of twin liquid crystals. Odd–even effects in the S_A-N^* transition temperatures are less common, but have been observed for some series of twin liquid crystals [15, 39] and also for main chain liquid crystalline polymers [11]. As with other twin liquid crystalline compounds, these effects attenuate with spacer length. The odd–even effects are strongest for compounds **III** and weaker for

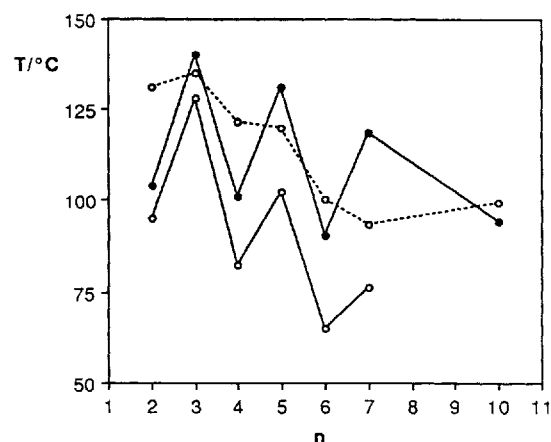


Figure 2. Dependence of the melting points (---○---), S_A-N^* (—○—) and N^*-I transition temperatures (—●—) on n , the number of methylene units in the alkanolate spacers of compounds **IV-*n***.

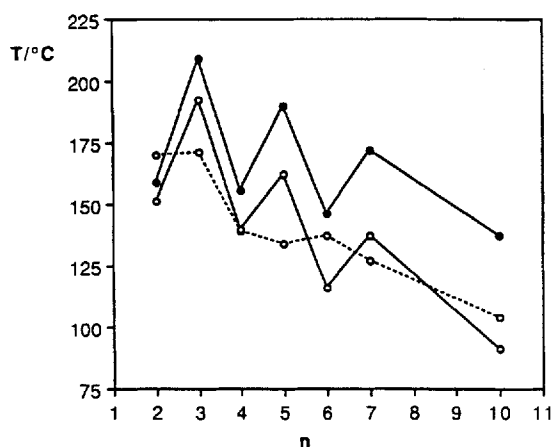


Figure 3. Dependence of the melting points (---○---), S_A-N* (—○—) and N*-I transition temperatures (—●—) on *n*, the number of methylene units in the alkanate spacers of compounds V-*n*.

compounds IV, but the differences between the series are not very prominent. The melting points of the compounds of the different series generally decrease with spacer length and here also an odd-even effect can be observed, although there are several exceptions. These are of course the result of different crystal packings for the different compounds in a series. In fact, for several compounds more than one crystalline form is found, resulting in different melting points for the same compound (see table 2).

The entropy changes ($\Delta S/R$) at the N*-I phase transitions of compounds III, IV and V show a strong odd-even effect (see table 2 and figure 4). The $\Delta S/R$ values of the S_A-I transitions of compounds III-1, IV-1 and V-1 are much larger than the values for the S_A-N* transitions of the other members of the series. This effect has also been found in for example the 4'-cyanobiphenyl-4-yl-

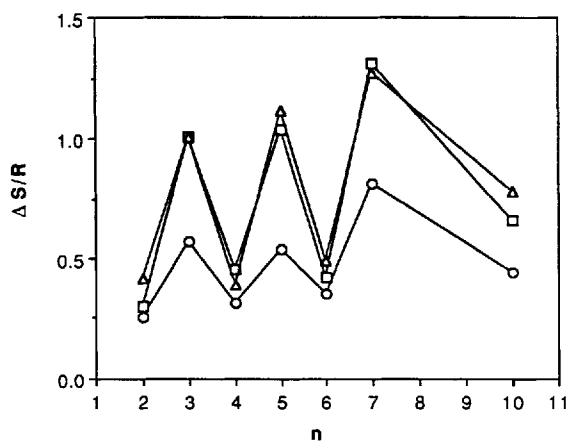


Figure 4. Dependence of the entropy change ($\Delta S/R$) of the N*-I transitions on the number of methylene units (*n*) in III-*n* (□), IV-*n* (○) and V-*n* (△).

oxyalkane series, but is absent in side chain liquid crystalline polymers with 4'-cyanobiphenyl-4-yl-oxyalkyl groups [5]. The $\Delta S/R$ values for the S_A-N* transitions of the present compounds vary only slightly with spacer length (see table 2) and for compounds IV and V no clear odd-even effects can be detected. The results for compounds III suggest that a small reverse odd-even effect is present for $\Delta S/R$ of the S_A-N* transition. This effect appears to be real, because the error in the $\Delta S/R$ values is estimated to be about ± 0.03 . For some series of main chain liquid crystalline polymers a reversed odd-even effect for the $\Delta S/R$ of the smectic-nematic transition has also been found [11]. The $\Delta S/R$ values of the N*-I transitions of the different odd and even series slightly increase with spacer length, but the odd-even effect does not seem to attenuate. From figure 4 it is clear that the odd-even effect for the compounds III and V is larger than that for compounds IV. The nature of the cholesteryl or dihydrocholesteryl group does not have a large influence on the odd-even effects in $\Delta S/R$. The odd-even effects are however smaller than those of the corresponding dimeric α,ω -bis-(4'-cyanobiphenyl-4-yloxy)alkanes [7, 12].

The odd-even effect in the physical properties of the nematic liquid crystalline phase of twin liquid crystals is usually ascribed to a difference in the preferred conformation of the compounds in this phase and its effect on the ordering in this phase [12-14, 40]. When the spacer is in the preferred all-*trans*-conformation, the rigid end groups give the molecule an overall syn- or anti-conformation, depending on the odd or even number of flexible units in the spacer. The anti-conformation of the molecules corresponds with a more condensed ordered phase, in which the directors of the mesogenic groups are oriented more or less parallel. In the present compounds, the number of flexible units equals the number of methylene groups in the spacer (*n*) plus two oxygens and one carbonyl group. The results for our compounds indicate that the compounds with odd *n* correspond to the most extended *trans*-like structure and the compounds with even *n* correspond with a more *cis*-like conformation when the alkyl spacers are in an all-*trans*-conformation. Crystal structure determinations of cholesteryl alkanates [41, 42] and molecular mechanics calculations (CHARMm) of compounds III-5 and III-6 seem to confirm this idea. It is therefore concluded that the chiral nematic phase has a higher degree of ordering for compounds with odd *n*. This is manifested by a higher N*-I transition temperature and a higher corresponding entropy change.

The much stronger odd-even effect in $\Delta S/R$ for the series with the 4'-cyanobiphenyl-4-yloxy mesogenic group than for the series with the 4-cyanophenoxy group indicates that the 4'-cyanobiphenyl-4-yloxy mesogenic unit is more important for the ordering of the nematic phase than the 4-cyanophenoxy group. Whether the other

mesogenic moiety is a cholesteryl or a dihydrocholesteryl group apparently has little influence on the ordering of the chiral nematic phase. This suggests that ordering is strongly influenced by stacking interactions between the aromatic groups. The smaller odd–even effects in the present compounds as compared to the corresponding α,ω -bis-(4'-cyanobiphenyl-4-yloxy)alkanes may be caused by the orientation of the cholesteryl group with respect to the spacer. It has been shown that the overall shape of the molecule in the all-*trans*-conformation has a strong effect on the magnitude of the odd–even effect [12].

The combined entropy changes of the S_A – N^* transitions, which hardly show an odd–even effect and of the N^* – I transitions, which show a pronounced odd–even effect suggest that the smectic phase also has a higher degree of ordering for the compounds with odd n , assuming that the entropies of the isotropic phases are similar.

Selective reflection of light occurs when its wavelength in the medium equals the pitch of the helical arrangement of the molecules in the chiral nematic phase. The temperature dependence of the pitch of chiral nematics has been the subject of much (theoretical) research [22, 23]. It is, however, still difficult to relate the molecular structure with the physical behaviour of the pitch [37, 38]. The influence of the different mesogen systems on the odd–even effects in the selective reflection wavelengths of the planar oriented chiral nematic phase of the present series of twin liquid crystalline compounds was studied by measuring the transmission spectra of the compounds as a function of temperature (see figures 5, 6 and 7).

The reflection wavelengths of compound **III-2**, **IV-2**, **IV-4** and **IV-6** could not be measured in this way, because they probably fall below 330 nm, where absorption by the aromatic system of the compounds and the glass slides

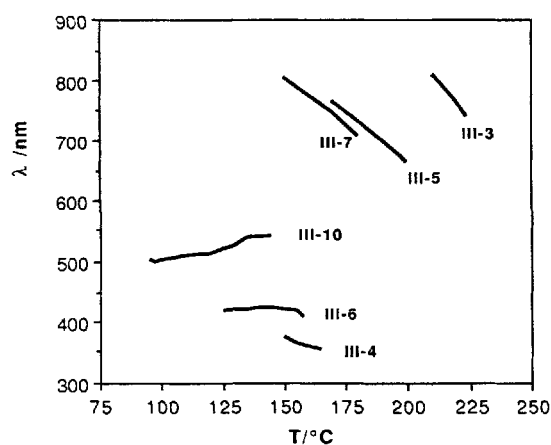


Figure 5. Dependence of the selective reflection wavelength on the temperature of compounds **III-*n*** in the chiral nematic phase.

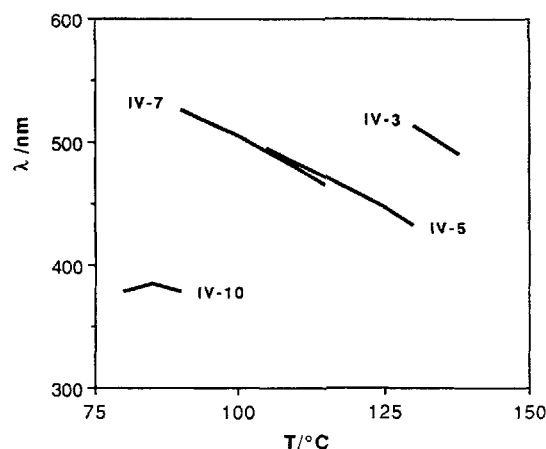


Figure 6. Dependence of the selective reflection wavelength on the temperature of compounds **IV-*n*** in the chiral nematic phase.

becomes important. The selective reflection wavelengths of **V-2** were not measured, because crystallization occurred before spectra could be measured.

As can easily be seen, the results for each of the three different series fall into two groups. The compounds with odd n reflect at a higher wavelength and this wavelength decreases with increasing temperature and spacer length. The reflection wavelengths of the compounds with even n are lower and increase with increasing spacer length. The reflection wavelengths for the compounds with even n are almost insensitive to temperature.

Although it is not possible to determine the reflection wavelengths of all pure compounds at the same temperature, it is apparent that there is a strong odd–even effect for the reflection wavelengths. This odd–even effect attenuates with increasing spacer length and also with temperature.

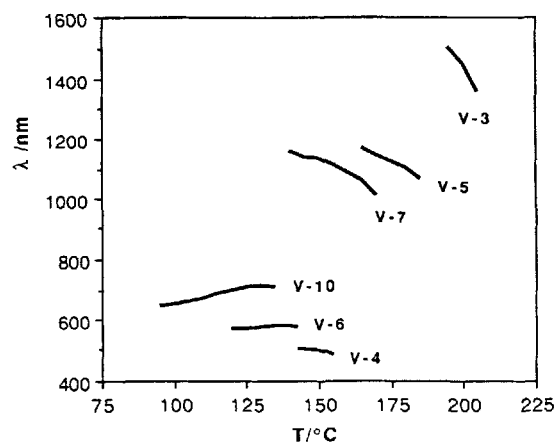


Figure 7. Dependence of the selective reflection wavelength on the temperature of compounds **V-*n*** in the chiral nematic phase.

For liquid crystals with a chiral centre in the alkyl chain, it was found that the helix sense alternates with the number of flexible units between the mesogenic core and the chiral centre [26–28]. It is therefore important to determine if for our compounds the helix sense also alternates with spacer length. This was investigated by studying contact preparations of the chiral nematic phases of a compound with an odd and an even n which showed no discontinuity in the texture under a polarization microscope. A contact preparation with a cholesteryl alkyl ester also showed no discontinuity in the texture. This means that all our new compounds have a left-handed screw sense like cholesteryl alkanoates [24]. This was confirmed by measuring the reflection wavelengths of the cholesteric phases of mixtures of compounds with odd and even n and of mixtures of these compounds with cholesteryl alkyl esters whose screw sense is known to be left-handed. The selective reflection wavelengths of these mixtures are intermediate between those of the pure compounds.

It seems logical to propose that molecules with a more *trans*-like ordered structure with parallel directors of the mesogens give rise to a smaller twist angle in the chiral nematic phase and therefore to a larger helical pitch. This effect has for example been observed for chiral substrates dissolved in nematics with increasing alkyl chain lengths [22–24, 30]. Although the nematic phase favours an extended all-*trans*-conformation of alkyl chains, a certain fraction of bent rotamers is always present [12–14]. This fraction will of course increase with increasing chain length and also with temperature. For our compounds with odd n , this leads to a less ordered chiral nematic phase and therefore a lower reflection wavelength. For the compounds with an even n this leads to more molecules with a parallel orientation of the directors of the mesogenic groups and therefore a higher reflection wavelength. This could explain the observed attenuation of the odd–even effect on the reflection wavelength with spacer length and also with temperature. Although not shown in figures 5, 6 and 7, it is observed that the reflection wavelengths rise sharply upon cooling the cholesteric phase within a few degrees of the S_A-N^* transition temperature. This effect is often observed and can be ascribed to an unwinding of the helical arrangement [37, 38].

Upon comparing the optical properties of the different series, it is easily seen that substitution of a cholesteryl group by a dihydrocholesteryl group gives chiral nematic phases with higher reflection wavelengths and therefore longer pitches (see figures 5 and 7). This effect of dihydrocholesteryl compounds as compared to cholesteryl compounds is ascribed to its lower helical twisting power. Substitution of a 4'-cyanobiphenyl-4-yloxy group by a 4-cyanophenoxy group gives compounds with chiral nematic phases that reflect at lower wavelengths (see

figure 6). Apparently this group decreases the pitch of the chiral nematic phase.

It can be argued that although helix formation is induced by the chiral part of the molecule, the aromatic mesogenic units have a preference for a straight nematic phase. When these aromatic moieties interact more strongly due to stacking dipole–dipole interactions, dimerization can occur. When a better interaction is possible, as in the case of a longer aromatic system or with an overall *trans*-conformation of the molecules, the twist angle decreases and a larger pitch is observed.

4. Conclusions

Our results on these novel series of chiral twin liquid crystalline compounds have shown that there is a strong odd–even effect with spacer length on the thermal transition temperatures and entropies and also on the selective reflection wavelengths. The ordering of the molecules in the chiral nematic phase plays an important role in these effects. The selective reflection wavelengths of the chiral nematic phases are also determined by the helical twisting power of the chiral part of the molecule and the nature of the aromatic mesogenic part. Stacking interactions between the aromatic mesogenic parts may also play an important role in the observed odd–even effects of the selective reflection wavelengths. The present results may be useful for understanding the relation between chemical structure, ordering and the selective reflection of light by the chiral nematic phase.

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