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Influence of spacer lengths on the properties of chiral triplet liquid crystals based on estradiol

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A series of 3-[ω-(4-cyanobiphenyl-4′-yloxy)alkyl] ethers of estradiol 17-[ω-(4-cyanobiphenyl-4′-yloxy)alkanoates] with variable spacers has been prepared as chiral triplet liquid crystals. The compounds show very broad range cholesteric phases and are transformed into cholesteric glasses at room temperature. They exhibit odd–even effects for their cholesteric–isotropic transition temperatures and the associated entropy changes as a function of spacer length. The odd–even effects are observed upon changing the parity of both the ester and of the ether spacer. The best ordering is observed for compounds with an even number of methylene groups both in the ester and the ether spacer. In these cases the three mesogen units are oriented more or less parallel when the alkyl spacers are in the all-*trans*-conformations. Odd–even effects are also observed for the selective reflection wavelength of the planar cholesteric phase, depending on the parity of both spacers. For several compounds with short spacers the selective reflection wavelength increases strongly with temperature, whereas for other compounds this is almost temperature independent.

1. Introduction

Liquid crystals usually consist of a rigid central part to which flexible chains have been attached [1, 2]. These rigid parts are most often aromatic in nature, although the first compounds that were recognized as liquid crystals contained cholesterol as the rigid moiety [3]. The liquid crystalline phase exhibited by these cholesterol containing compounds has been called cholesteric, but is in fact a chiral nematic phase. The molecules in this phase are present in a helical arrangement, the pitch of which can be in the range of the wavelength of visible light. This causes the iridescent colours of these phases, and planar ordered films of these materials selectively reflect a single band of the spectrum. The cholesteric phase is a result of the chiral nature of the cholesterol group. For most other chiral liquid crystals, the chirality stems from a chiral centre in a flexible side chain [3]. Apart from cholesterol and dihydrocholesterol, several other rigid chiral steroids have been investigated for their liquid crystalline properties [4–8]. The liquid crystalline temperature range is often short and the occurrence of liquid crystalline properties appears to depend strongly on the substitution patterns and positions of the double bonds.

In general, small structural changes can have drastic effects on the liquid crystalline properties. Twin or dimer liquid crystals, for example, consisting of two rigid mesogenic units connected by a flexible alkyl spacer are characterized by a strong alternating behaviour of the nematic–isotropic transition temperatures and the associated entropy changes as a function of spacer length [9–14]. When the number of flexible units in the spacer is even, the rigid mesogenic groups preferably adopt a parallel orientation in the nematic phase. This gives better ordered nematic phases that have higher isotropization temperatures and higher corresponding entropy changes than homologues with an odd number of flexible units in the spacer [15–18]. These odd–even effects on the isotropization temperature and corresponding entropy change have also been found for some chiral twin liquid crystals [19–24].

The selective reflection wavelength of the cholesteric phase, which is directly related to the helical pitch, also depends on the ordering of the molecules in the liquid crystalline phase [3, 25, 26], and odd–even effects in the optical properties of some series of chiral twin liquid crystals containing a dihydrocholesteryl mesogenic unit are indeed found [27, 28].

Twin liquid crystals can be considered as model compounds for main chain liquid crystalline polymers [13, 14]. This can also be said for triplet liquid crystals consisting of three mesogenic units separated by two flexible units, and some series have recently been

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investigated and shown to exhibit odd–even effects [9, 29–32]. Chiral triplet liquid crystals consisting of a central biphenyl mesogen and chiral dihydrocholesteryl groups as terminal mesogen units connected via flexible alkanoate spacers also exhibit an odd–even effect as a function of the parity of both spacers [33]. Odd–even effects were found as a function of spacer length for the cholesteric–isotropic transition temperature (T_{N^*-I}), the associated entropy change ($\Delta S/R$) and the selective reflection wavelength. In this series of triplet liquid crystals, the aromatic group is in the centre and the bulky steroids are at the termini. Because the ordering properties of liquid crystalline phases strongly depend on the intermolecular interactions between their mesogens, it can be argued that triplets with a central bulky steroid and two terminal aromatic mesogens might have very different properties.

Therefore, we wished to extend this study by investigating triplet liquid crystals containing a central bifunctional steroid mesogen. Androstenol [6,34] and estradiol [35–39] have been used as bifunctional chiral mesogenic moieties in liquid crystals. Recently, we investigated estradiol derivatives containing two terminal cyanobiphenyl mesogens connected by identical alkanoate spacers. For these compounds, no strong odd–even effects were found, probably because the preferred orientation of the terminal mesogens is never parallel [40]. In this paper we report on the properties of a series of estradiol based triplets containing an ester and an ether linked spacer in which the spacer length can easily be varied independently.

2. Experimental

2.1. *Synthesis*

A mixture of 544 mg (2 mmol) of β-estradiol, 3 mmol of the appropriate dibromoalkane and 1·5 g of anhydrous potassium carbonate in 30 ml of butanone was heated at reflux for 40 h. After cooling, the solvent was evaporated, dichloromethane was added and the salts were removed by filtration. The filtrate was concentrated and the residue was purified by column chromatography on silica gel with dichloromethane/methanol 200 : 1 (v/v) as eluent. Yields: 70–80 per cent. Compound **I-6**: ^{1}H-NMR ($CDCl_3$) δ 7·2 (d, 1H, Ar estradiol), 6·65 (m, 2H, Ar estradiol), 3·9 (t, 2H, CH_2O), 3·7 (t, 1H, CHOH), 3·4 (t, 2H, CH_2Br), 2·9–1·0 (m, 23H, aliphatic), 0·75 (s, 3H, CH_3).

The monohydroxy compound **I-n** (1 mmol) was dissolved in a mixture of 2 ml of pyridine and 4 ml of benzene. After cooling to 5°C a solution of the appropriate ω-bromoalkanoyl chloride (1·5 mmol) in 3 ml of benzene was added. The mixture was stirred for 1 h at 5°C and 1 h at ambient temperature. After addition of 20 ml of dichloromethane the mixture was washed with three 25 ml portions of 1 M HCl, dried with $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel with dichloromethane as eluent. Yields: 70–80 per cent. Compound **II-6,7**: ^{1}H NMR ($CDCl_3$) δ 7·2 (d, 1H, Ar estradiol), 6·65 (m, 2H, Ar estradiol), 4·7 (m, 1H, CHO), 3·9 (t, 2H, CH_2O), 3·4 (t, 4H, CH_2Br), 2·9–1·2 (m, 35H, aliphatic), 0·8 (s, 3H, CH_3).

A mixture of the dibromo compound **II-n,m** (0·5 mmol), 4-(4-cyanophenyl)phenol (1·5 mmol) and 1 g of anhydrous potassium carbonate in 20 ml of butanone was heated at reflux for 40 h. After cooling, the solvent was evaporated, dichloromethane was added and the salts were removed by filtration. The filtrate was concentrated and the residue was purified by column chromatography on silica gel with dichloromethane as eluent and on deactivated aluminium oxide (activity III) with dichloromethane/hexane 2 : 1 (v/v) as eluent. Yields: 30–40 per cent. Compound **III-6,7**: ^{1}H NMR ($CDCl_3$) δ 7·7 (m, 8H, Ar biphenyl), 7·55 (m, 4H, Ar biphenyl), 7·2 (m, 1H, Ar estradiol), 7·0 (m, 4H, Ar biphenyl), 6·7 (m, 2H, Ar estradiol), 4·7 (t, 1H, CHO), 4·0 (m, 6H, OCH_2), 2·9–1·3 (35H, aliphatic), 0·8 (s, 3H, CH_3). Elemental analysis: Calculated ($C_{58}H_{64}N_2O_5$) C: 80·15; H: 7·42; N: 3·22; Found C: 80·44; H: 7·72; N: 3·04 per cent.

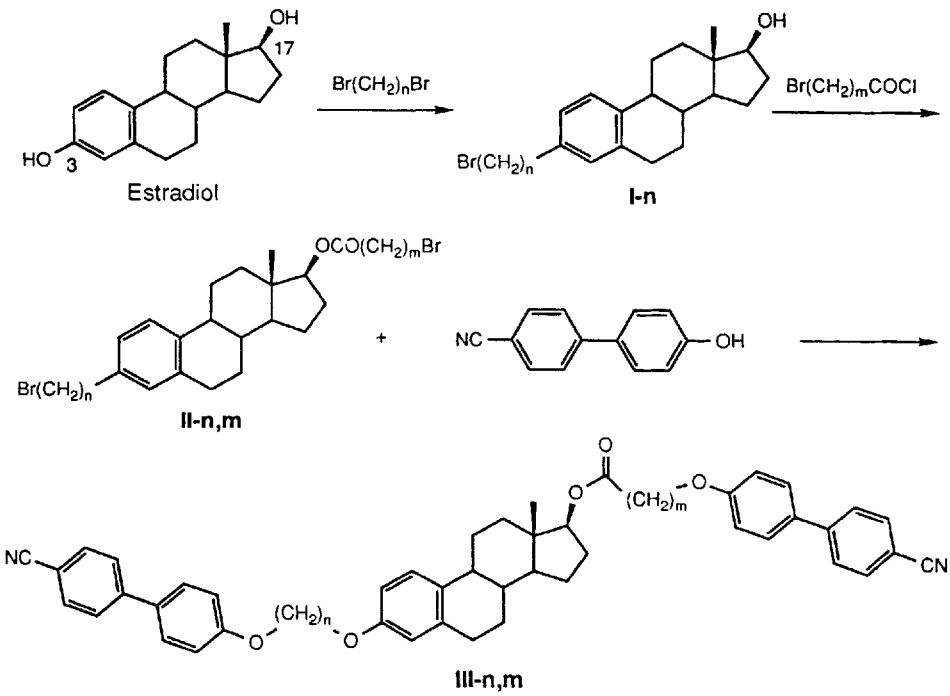
2.2. *Measurements*

Measurement of melting points and phase transition temperatures and optical inspection of the liquid crystalline phases were made on samples mounted between ordinary glass slides using an Olympus BH-2 polarization microscope equipped with a Mettler FP82HT hot stage, which was controlled by a Mettler FP80HT central processor. 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 in the measuring beam of a Hewlett Packard 8452A photodiode array or a Cary 5E UV/VIS/NIR spectrophotometer. Differential scanning calorimetry (DSC) thermograms were obtained on a Perkin Elmer DSC-7 system using 3–7 mg samples in 50 µl sample pans at a scan rate of 10°C min^{-1}. 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 expressed in J mol^{-1} and T is the corresponding phase transition temperature in Kelvin.

3. Results and discussion

3.1. *Synthesis*

The synthesis of the compounds is presented in the scheme. The approach used for the synthesis of the triplet liquid crystals affords a simple means of independently varying the spacer lengths. The two hydroxy groups



Scheme.

of β-estradiol are different and the phenolic group at the 3-position can be selectively converted into an ether to give compounds **I-n**. The remaining hydroxy group at the 17-position is then converted into an ester **II-n,m** by reaction with an ω-bromoalkanoyl chloride. Finally the dibromo compounds **II-n,m** are reacted with 4-(4-cyanophenyl)phenol to give the triplets **III-n,m**. The final products were purified by column chromatography on different chromatographic systems until good ^{1}H NMR spectra and single spots on alumina and silica gel thin layer chromatograms were obtained. The compounds gave good C, H and N elemental analyses. After isolation, the compounds appear to be hard to crystallize and are usually isolated as glasses at room temperature. Only upon prolonged storage at elevated temperatures does crystallization occur.

3.2. *Thermal properties*

In figure 1, the DSC thermogram of compound **III-7,4** is given. The second heating and cooling curves are displayed. In both traces the glass transition and the cholesteric–isotropic transition are clearly visible. The table gives the melting points, T_{N^*-I} and corresponding $\Delta S/R$ values and glass transition temperatures (T_g) of compounds **III-n,m**. The compounds can easily be cooled to room temperature without crystallization. The asymmetric nature of the estradiol moiety, coupled with the identical terminal mesogenic groups of the molecules probably prevents easy crystallization. The T_g values

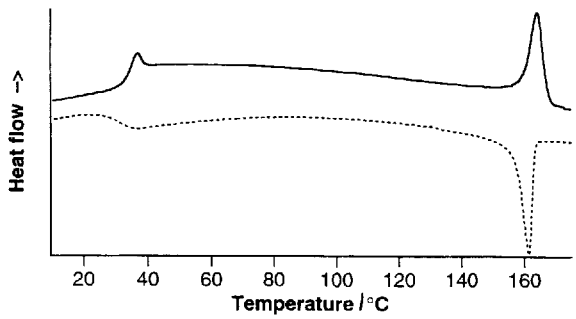


Figure 1. DSC thermograms of the second heating (solid line) and cooling (broken line) cycles for **III-7,4**.

decrease with increasing spacer length as would be expected. Although in principle all compounds produce glasses when they can be supercooled enough below their melting point, it is seldom observed that non-polymeric compounds produce glasses at room temperature [41, 42]. Interestingly, some other estradiol-based liquid crystals also form glasses at room temperature [38, 39].

The cholesteric phases that are observed are very broad range (see also figure 1) and no smectic phases are found except for **III-7,5** which has an S_A–N* phase transition at 60°C. The asymmetrical nature of the estradiol moiety and the fact that the central estradiol moiety has a cross-sectional area that is much larger

Table. Melting points (m.p.), chiral nematic–isotropic (N*→I) phase transition and glass transition (T_g) temperatures (°C) of compounds **III-n,m.** The entropy change $\Delta S/R$ at the chiral nematic–isotropic transition is in square brackets.

Compound	m.p.	T_{N^*-I}		T_g
III-5,4	158	166	[1·46]	40
III-5,5	74	146	[0·90]	30
III-5,6	81	139	[1·23]	30
III-6,3	185	(184)[b]	[1·90]	39
III-6,4	150	193	[3·03]	37
III-6,5	141	177	[2·02]	31
III-6,6	118	179	[2·82]	29
III-6,7	136	168	[2·35]	25
III-7,4	160	163	[1·60]	32
III-7,5[a]	120	150	[1·07]	27
III-7,6	69	141	[1·44]	26

[a] This compound has an additional S_A–N* transition at 60°C.

[b] Round brackets indicate a monotropic transition.

than that of the alkyl and aromatic groups may be the reasons that layered smectic phases are not easily formed.

From the table and figure 2 it is seen that for compounds with $n=6$, a small but distinct odd–even effect is found for the nematic–isotropic transition temperatures as a function of the spacer length m. For compounds with $n=5$ or $n=7$, probably a small odd–even effect is also present for T_{N^*-I}. Upon comparing compounds with equal spacers m, the odd–even effect is very clear. This indicates that changing the spacer length on the 3-ether side of the molecule has a stronger effect on the ordering than a change in spacer length on the 17-ester side. The same effect was observed previously for bis-ester triplet liquid crystals of estradiol in which the parity of the spacer at the 3-position has a larger effect on the ordering than the parity of the spacer at the 17-position [40]. The difference is therefore not completely caused by the difference in linkage, but also by the site of attachment to the estradiol. In general the nature of the linkage has been found to have a strong influence on the odd–even effect; for example, compounds with direct CH_2 linkages give larger odd–even effects than compounds with ether linkages [8, 15].

The influence of the parity of the spacer on the transitional properties are more clearly displayed in the entropy change ($\Delta S/R$) at the N*–I transition (figure 3 and table). For the compounds with $n=6$, a clear odd–even effect is seen depending on the parity of the m-spacer. This effect attenuates with increasing spacer length. Compounds **III-5,4, III-5,6, III-7,4** and **III-7,6** have a higher $\Delta S/R$ than the compounds of the same series with odd m, **III-5,5** and **III-7,5**. Upon changing n for compounds with the same m, the odd–even effect is also clearly seen. From figure 2 and especially from figure 3, it can be concluded that the compounds **III-6,4** and **III-6,6** have the highest nematic ordering, and compounds **III-5,5** and **III-7,5** have the lowest nematic ordering of this series. The other compounds have an intermediate ordering, but compounds with even n have a higher ordering than compounds with odd n.

The spacer at the 3-position has 8 flexible units for compounds with $n=6$. Therefore, the aromatic groups connected by this spacer have a parallel orientation when the spacer is in the all-*trans*-conformation. The expected higher ordering corresponds nicely with the

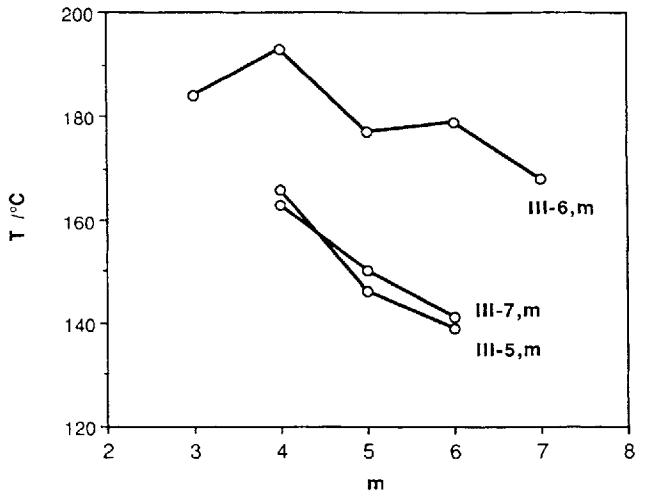


Figure 2. Dependence of the N*–I transition temperatures of compounds **III-n,m** on the length of the spacer m. Points for compounds with the same m have been connected.

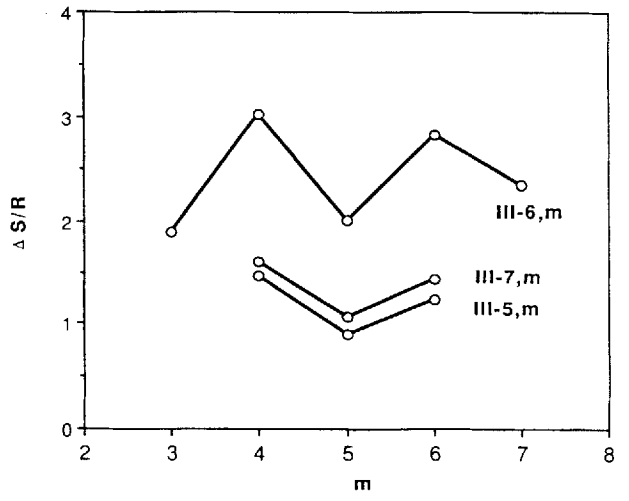


Figure 3. Dependence of the entropy change $\Delta S/R$ at the N*–I transition of compounds **III-n,m** on the length of the spacer m. Points for compounds with the same m have been connected.

observed higher isotropization temperatures and the corresponding entropy changes for these compounds.

The spacer at the 17-position however has $m+3$ flexible units (m CH_2 groups, two oxygens and one carbonyl group). At first sight it seemed rather puzzling that compounds with even m (and an odd number of flexible units) have better ordered cholesteric phases than compounds with odd m. Inspection of the 3-dimensional structure of β-estradiol derivatives [43, 44] reveals that the phenolic 3-OH group is approximately parallel with the long axis of the estradiol moiety, whereas the aliphatic 17-OH group makes a large angle with this moiety. This means that for an odd number of flexible units at the 17-position the estradiol and the cyanobiphenylyl groups are preferentially oriented parallel in the nematic phase.

3.3. *Optical properties*

The molecules in the cholesteric phase are present in a helical arrangement and the pitch of the helix is influenced by the ordering of the molecules in the phase [3, 25, 26]. This can be studied by measuring the selective reflection of light by the planar ordered cholesteric phase, because the wavelength of the reflected light in the liquid crystalline phase is related to the pitch of the cholesteric helix. Therefore measurement of the selective reflection wavelength can in principle give information about the ordering of the phase as a function of temperature, whereas measurement of $\Delta S/R$ only provides information about the ordering change at the isotropization temperature. Examination of the selective reflection wavelength of mixtures of these compounds and of mixtures of these compounds with cholesterics with known screw sense shows that the compounds have a left-handed screw sense, independent of the parity of the spacers.

Figures 4–6 show the selective reflection wavelengths of the triplets as a function of temperature. It is evident that several compounds have a strong temperature dependence for their selective reflection wavelength, whereas the selective reflection wavelength of others is almost temperature independent. The compounds with $m=4$ of the series **III-5,m** and **III-7,m** (figures 4 and 5) show an increase of the selective reflection wavelengths with temperature. The compounds with $m=5$ or 6 have a temperature independent reflection wavelength. For these series with odd n, a clear odd–even effect is observed in which the compounds with $m=5$ have the lowest selective reflection wavelength. From the transitional properties, we have seen that these compounds have the lowest ordering. These results are in agreement with the findings for other chiral twin and triplet liquid crystals, where a lower ordering corresponds with a lower selective reflection wavelength [27, 28, 33].

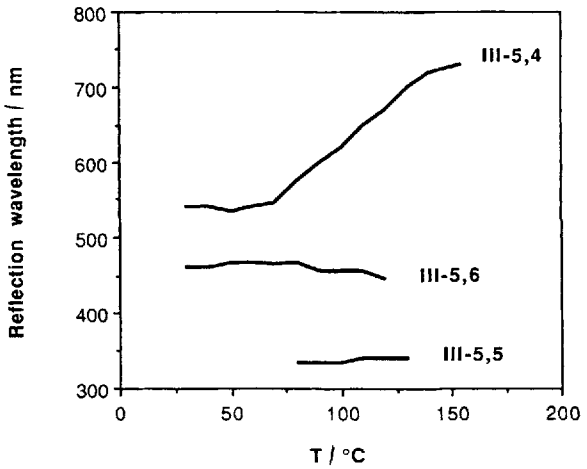


Figure 4. Dependence of the selective reflection wavelength on temperature for compounds **III-5,m** in the chiral nematic phase.

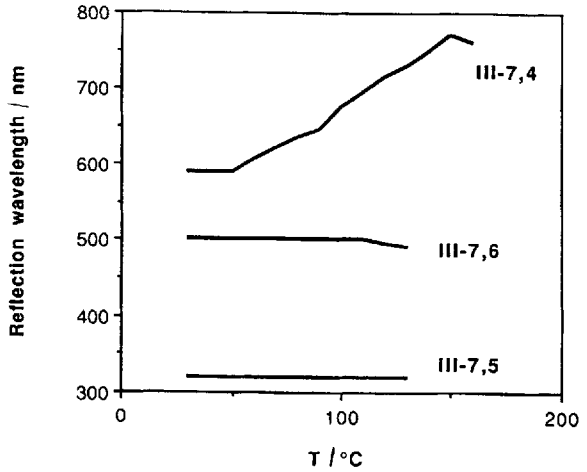


Figure 5. Dependence of the selective reflection wavelength on temperature for compounds **III-7,m** in the chiral nematic phase.

For the compounds with $n=6$ the selective reflection wavelengths increase with temperature except for **III-6,6** for which the reflection wavelength is almost temperature independent (see figure 6). For this series of five compounds it is clearly seen that the selective reflection wavelength shows an odd–even effect with the parity of the spacer m and that this effect attenuates with the spacer length. The selective reflection wavelength of **III-6,4** and **III-6,6** is much higher than for the other compounds. From the transitional properties it was concluded that these compounds have the highest ordering of this series. Again this agrees with what was found for other chiral twin and triplet liquid crystals [27, 28, 33].

The temperature dependence of these β-estradiol derivatives is completely different from that of derivatives

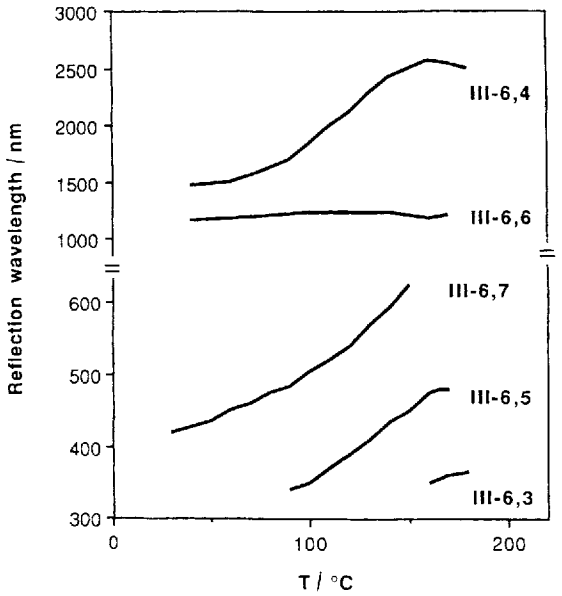


Figure 6. Dependence of the selective reflection wavelength on temperature for compounds **III-6,m** in the chiral nematic phase. The upper part of the figure has a different scale for the selective reflection wavelength.

of cholesterol or dihydrocholesterol. Of course a different chiral mesogen is present which might cause the different temperature behaviour [4]. It has been found that each chiral centre has its own temperature dependence, which contributes to the overall temperature dependence of the pitch [45, 46]. However, the temperature dependence of compounds **III-6,4** and **III-6,6** suggests that for these compounds a different change of temperature dependent ordering of the phase takes place. This change in temperature dependent behaviour is also manifested for the pair **III-5,4** and **III-5,6** and the pair **III-7,4** and **III-7,6**. In all cases the compounds with the longer spacer *m* show a temperature independent behaviour, whereas the compounds with the shorter spacer *m* show a strong temperature dependence. Perhaps a longer spacer stabilizes the low temperature ordering. A change in ordering could be caused by a change in the intermolecular interactions between the molecules, for example stacking interactions or dimer formation [26], or a change in conformation of the molecules, such as a rotation about a single bond that influences the orientation of the estradiol unit with respect to the orientation of the cyanobiphenylyl groups. A candidate for this would be a rotation that changes the orientation of the carbonyl group. A decrease of the selective reflection wavelength with lower temperature has been ascribed before to an increase in ordering [47].

4. Conclusions

We have prepared a series of chiral triplet liquid crystals containing a central estradiol mesogenic unit and two terminal cyanobiphenylyl mesogenic moieties connected by flexible spacers. Because the estradiol is linked at the 3-position to the spacer via an ether linkage and at the 17-position via an ester linkage, the lengths of the alkyl spacers can be varied independently. Almost all compounds exhibit very broad range cholesteric phases, which extend to below room temperature. Glass transition temperatures are observed slightly above room temperature. This prevents an easy crystallization of the cholesteric glasses. Odd–even effects are observed as a function of the parity of the spacers for the isotropization temperature and the associated entropy change. The highest ordering, reflected by a high isotropization temperature and a high associated entropy change is found for molecules which have all three mesogenic units in a parallel orientation when the spacers are in the preferred all-*trans*-conformation.

Odd–even effects are also observed for the selective reflection wavelengths. Compounds with the highest ordering give the highest selective reflection wavelengths. It was found that the parity of the spacer at the 3-position has a larger effect on the ordering of the cholesteric phase than the parity of the 17-spacer. The temperature dependence of the selective reflection wavelength was investigated. Several compounds, usually those with the shorter spacers have a strong temperature dependence, which sometimes spans almost the entire visible light region. Other compounds, however, exhibit an almost temperature independent selective reflection wavelength. The reason for this different behaviour might be associated with a temperature dependent change in conformation or a change in intermolecular interactions of the molecules.

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