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Odd–even effects in the thermotropic and optical properties of chiral triplet liquid crystals

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A series of chiral triplet liquid crystalline compounds with a central biphenyl group to which two dihydrocholesteryl groups are attached via two flexible alkanoate spacers has been prepared and investigated. As a function of spacer length, these compounds show strong odd–even effects for the phase transition temperatures, the corresponding entropy changes and the selective reflection wavelengths associated with the chiral nematic phases. Asymmetrical compounds with one odd and one even number of methylene groups in their spacers have properties intermediate between those of symmetrical compounds with two odd or two even spacers.

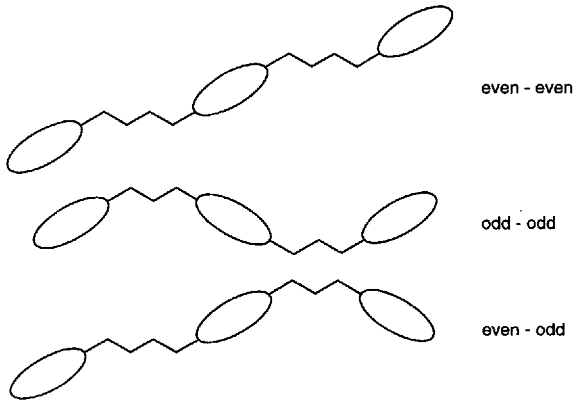
1. Introduction

Thermotropic liquid crystalline compounds usually consist of a rigid central part called mesogenic core, to which flexible chains are attached [1, 2]. Molecules that are composed of two mesogenic units connected by a flexible spacer constitute a different class of liquid crystals [3–16]. These so-called twin or dimer liquid crystals have been recognized as models for main chain liquid crystalline polymers [17, 18] because both types of liquid crystalline compounds exhibit a fascinating alternating behaviour of the physical properties associated with the nematic phase as a function of spacer length.

Recently it has been suggested that the transitional properties of side chain liquid crystalline polymers can be accounted for by a virtual trimer model [19, 20]. It was found that the clearing temperatures and entropy changes of a homologous series of model trimer or triplet liquid crystals in which three mesogenic units are connected by two identical flexible spacers exhibit a strong odd–even effect [19].

The odd–even effects in the transitional properties are associated with the differences in ordering of the mesogens in the nematic phase [21–23]. Twin liquid crystalline compounds with an even number of flexible units in their spacer have an overall *trans*-like conformation with a parallel orientation of the directors of the mesogenic units and therefore have a better ordering of their nematic phase than compounds with an odd number of flexible units in their spacers. This odd–even effect is observed for the nematic–isotropic phase transition temperatures and the associated entropy changes, and recently we have also observed strong odd–even effects for the selective reflection wavelengths of the chiral nematic phases of chiral twin liquid crystals [24, 25].

Addition of a third mesogenic unit gives molecules in which the directors of all three mesogenic moieties are parallel for compounds with two even spacers. From scheme 1 it is clear that compounds with two odd numbers of flexible units in their spacers may also have their terminal mesogenic units parallel, whereas the central mesogenic unit has a different orientation.



Scheme 1.

For compounds with one even and one odd spacer the directors of the central and one of the terminal mesogenic groups are parallel and one of the terminal mesogenic units has a different orientation. Due to these conformations, it is not a priori clear if compounds with two odd or compounds with one odd and one even spacer have the poorer ordering, because in both types of compound two mesogenic units have their directors parallel when the

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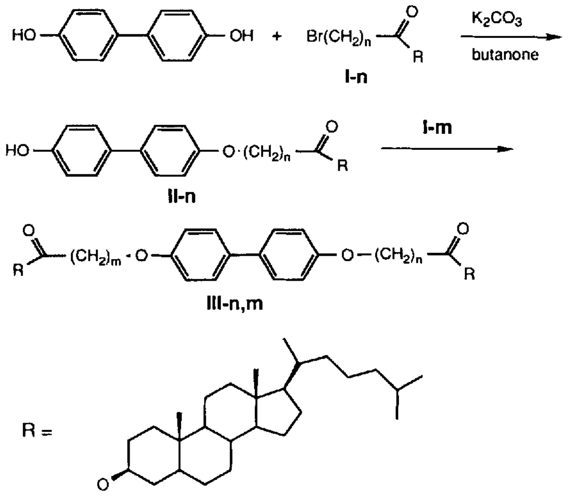
flexible units in the spacers are in the preferred all-*trans*-conformation.

Because of our recent interest in chiral twin liquid crystals [24, 25] and because further information on the ordering of the chiral nematic phase can be obtained from the selective reflection wavelengths [26–28], we set out to investigate the ordering properties of a series of chiral triplet liquid crystals, consisting of a central biphenyl group to which two chiral dihydrocholesteryl mesogenic groups are attached via flexible alkanoate spacers, by determining the thermotropic and optical properties as a function of spacer length. Only a few examples of triplet liquid crystals have been reported in the literature [29–32], but only achiral compounds and compounds with symmetrical spacers have been investigated. In all cases odd–even effects have been observed, especially for the N–I transition temperatures.



Scheme 2.

2. Experimental

2.1. *Synthesis*

2.1.1. *Dihydrocholesteryl ω-(4′-hydroxybiphenylyloxy)-alkanoates* II

A mixture of 1 mmol of 4,4′-biphenol, 1 mmol of the appropriate dihydrocholesteryl ω-bromoalkanoate **I** [25, 33] and 1 g of anhydrous potassium carbonate in 20 ml of butanone was heated under reflex for 16 h. After filtration of the salts and evaporation of the solvent, the residue was separated by column chromatography on silica gel using dichloromethane as eluent. First a fraction of symmetrically bis-substituted product **III** was obtained (25 per cent) and secondly a fraction of **II** (60 per cent) was obtained, which was purified by recrystallization from acetone. **II-7**: ^{1}H NMR ($CDCl_3$) δ 7·4 (m, 4 H, aromatic), 6·9 (m, 4 H, aromatic), 5·3 (s, 1 H, OH), 4·7 (m, 1 H, $C\underline{H}O$), 4·0 (t, 2 H, $C\underline{H}_2O$), 2·3 (t, 2 H, $C\underline{H}_2C{=}O$), 2·0–0·6 (m, 65 H, aliphatic). Elemental analysis, calculated ($C_{50}H_{70}O_4.H_2O$): C, 79·74; H, 10·07, found: C, 79·74; H, 9·64 per cent **III-7,7**: ^{1}H NMR ($CDCl_3$) δ 7·4 (d, 4 H, aromatic), 6·9 (d, 4 H, aromatic), 4·7 (m, 2 H $C\underline{H}O$), 4·0 (t, 4 H, $C\underline{H}_2O$), 2·3 (t, 4 H, $C\underline{H}_2C{=}O$), 2·0–0·6 (m, 112 H, aliphatic). Elemental analysis calculated ($C_{82}H_{130}O_6$): C, 80·97; H, 11·07: found: C, 81·27; H, 10·81 per cent.

2.1.2. *Symmetrically substituted compounds* III

A mixture of 2·1 mmol of the appropriate dihydrocholesteryl ω-bromoalkanoate **I**, 1 mmol of 4,4′-biphenol and 1 g of anhydrous potassium carbonate in 20 ml of butanone was heated under reflux for 16 h. After filtration of the salts and evaporation of the solvent, the residue was purified by column chromatography on silica gel, using dichloromethane as eluent, and recrystallization from petroleum ether, b.p. 60–80°C. Yields 80–90 per cent.

2.1.3. *Asymmetrically substituted compounds* III

A mixture of 1 mmol of **II**, 1 mmol of the appropriate dihydrocholesteryl ω-bromoalkanoate **I** and 1 g of anhydrous potassium carbonate in 20 ml of butanone was heated under reflux for 16 h. After filtration of the salts and evaporation of the solvent, the residue was purified by column chromatography on silica gel, using dichloromethane as eluent, and recrystallization from petroleum ether b.p. 60–80°C. Yields 80–90 per cent.

2.2. *Measurements*

Melting points and thermal phase transition temperatures were determined and optical inspection of the liquid crystalline phases was 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 mounted between parallel glass slides in the measuring beam of a Hewlett Packard 8452A diode array 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 $\Delta S/R$, where 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

The synthetic routes employed for synthesizing the triplets **III** are straightforward and allow easy synthesis of compounds with asymmetric spacers (see scheme 2). Compounds with symmetric spacers are easily prepared in high yield from 4,4′-biphenol and two molar equivalents of **I**. The structures and purity of all new compounds were confirmed by ^{1}H NMR, by single spot behaviour on thin

Table 1. Melting points (m.p.), smectic A–chiral nematic ($S_A \rightarrow N^*$) and chiral nematic–isotropic ($N^* \rightarrow I$) phase transition temperatures (°C) of compounds **II**-*n* and **III**-*n*, *m*. Transition temperatures for monotropic phases are in parenthesis. The corresponding entropy changes $\Delta S/R$ in square brackets.

Compound	m.p.		$S_A \rightarrow N^*$		$N^* \rightarrow I$	
II-4	172	[8·3]	†		†	†
II-5	159	[8·8]	(156)	[0·56]	172	[1·56]
II-7	140	[8·9]	(130)	[0·31]	146	[1·77]
III-4,4	183	[16·0]	†		183	[0·81]
III-4,5	170	[9·9]	†		207	[1·43]
III-4,6	152	[9·2]	†		172	[0·65]
III-5,5	178	[9·6]	178	[0·05]	227	[2·50]
III-5,6	151	[15·5]	†		198	[1·43]
III-5,7	155	[9·3]	179	[0·05]	212	[2·47]
III-6,6	157	[13·6]	†		167	[0·77]
III-6,7	154	[17·5]	†		184	[1·51]
III-7,7	152	[16·8]	170	[0·12]	196	[2·61]
III-10,10	133	[9·2]	†		153	[0·93]

† Not observed.
Parentheses indicate a monotropic transition.

layer chromatograms and by correct C and H elemental analyses.

The melting points, smectic A–chiral nematic (S_A–N^*) and chiral nematic–isotropic (N^*–I) phase transition temperatures of the compounds **II** and **III** are given in the table.

Compounds **II-5** and **II-7** give enantiotropic N^*–I phase transitions and monotropic S_A–N^* transitions. Upon applying mechanical stress to the S_A phases of compounds **II-5** and **II-7** between glass slides, a highly aligned homeotropic phase is obtained.

All of the compounds **III** show chiral nematic phases with enantiotropic N^*–I phase transitions; a S_A phase is observed for only a few of the compounds, namely those with two odd numbers of methylene units (*n*, *m*) in their spacers. Due to the steric requirements of the different mesogenic units, it is not easy to imagine a smectic phase for these molecules with a stacking of the aromatic groups. This may be the reason that for these compounds broad nematic ranges are found and that for most compounds no smectic phase is observed.

The N^*–I phase transition temperatures are graphically represented in figure 1. The compounds with odd–odd (*n*, *m*) have the highest N^*–I phase transition temperatures and compounds with even–even (*n*,*m*) have the lowest N^*–I phase transition temperatures. The compounds with odd–even (*n*, *m*) have intermediate phase transition temperatures. Within each series, the N^*–I phase transition temperatures decrease with spacer length.

The entropy changes (expressed as $\Delta S/R$) of the phase transitions of compounds **III** are given in the table. Only for the compounds with odd–odd (*n*, *m*) is a S_A phase found with a very low $\Delta S/R$ value. The entropy changes of the N^*–I phase transitions are also graphically represented in figure 2.

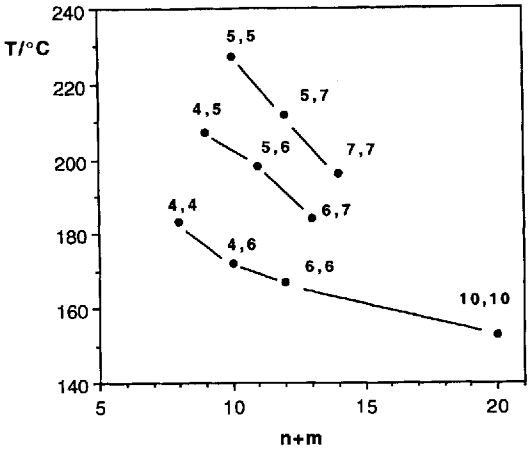


Figure 1. Plot of the N^*–I phase transition temperature (●) of compounds **III**-*n*, *m* as a function of $n + m$, the total number of methylene units in the spacers.

Here again the results fall into three groups. Compounds with odd–odd (*n*, *m*) have the highest $\Delta S/R$ values. The compounds with even–even (*n*, *m*) have the lowest $\Delta S/R$ values and the compounds with odd–even (*n*, *m*) have intermediate $\Delta S/R$ values. Within the groups, the $\Delta S/R$ values seem to increase slightly with spacer length. The results can be regarded as an odd–even effect for the compounds with odd–odd and even–even (*n*, *m*). Compounds with odd–even (*n*, *m*) show intermediate values.

The odd–even effect in the physical properties of twin liquid crystals is usually ascribed to a difference in the preferred conformation of the compounds in the nematic phase and its effect on the ordering in this phase [21–23, 34]. When the alkyl spacer is in the preferred

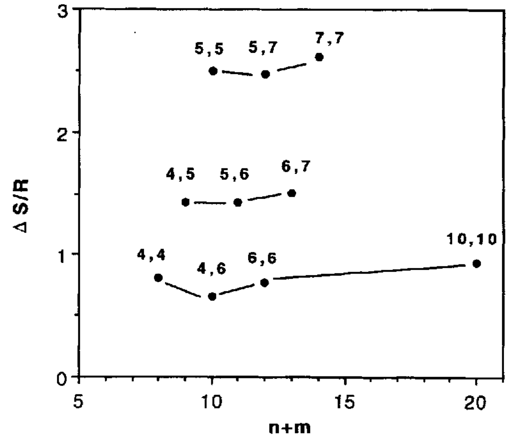


Figure 2. Plot of the entropy changes ($\Delta S/R$) of the N^*–I phase transitions (●) of compounds **III**-*n*, *m* as a function of $n + m$, the total number of methylene units in the spacers.

all-*trans*-conformation, the rigid end groups give these molecules an overall *syn*- or *anti*- conformation, depending on the odd or even number of flexible units in the spacer. The *anti*-conformation of these molecules corresponds with a more condensed ordered phase, in which the directors of the mesogenic groups are oriented more or less parallel. The results of a similar reasoning for our triplet compounds are schematically represented in scheme 1. An odd n or m in our compounds means that there are an even number of flexible units in the spacer (the number of methylene groups plus two oxygens and a carbonyl group). It is seen that the compounds with odd–odd (n, m) therefore correspond to the most extended *trans*-like structure with the more condensed and better ordered phase. Studies on cholesteryl ω-(4′-cyanobiphenyl-4-yloxy)alkanoates confirm the idea that compounds **III** with an odd–odd (n, m) give the better ordered chiral nematic phases [24, 25]. This results in the highest N*–I phase transition temperatures and $\Delta S/R$ values.

The lower N*–I phase transition temperatures (see figure 1) and the lower $\Delta S/R$ values (see figure 2) of compounds **III** with even–even (n, m) indicate that they have a poorer ordering in their nematic phase that the compounds with odd–even (n, m). This also suggests that the triplets with odd–even (n, m) effectively behave as a mixture of odd and even twins with respect to their thermotropic properties. Apparently a better ordered nematic phase is obtained when the directors of the central biphenyl and one of the dihydrocholesteryl groups are parallel than when the directors of the two terminal dihydrocholesteryl groups are parallel. It can be argued that the poor ordering in compounds with even–even (n, m) results from two alternations in the orientation of their mesogenic units, whereas in compounds with odd–even (n, m) there is only one alternation in the orientations of the mesogenic groups (see scheme 1). It is also possible that the aromatic group is more important for ordering than the dihydrocholesteryl group and that therefore a parallel orientation of the biphenyl group and a dihydrocholesteryl group contributes more to the ordering than the parallel orientation of two dihydrocholesteryl groups. In the chiral nematic phase, the molecules are present in a helical arrangement and the pitch of this helix is influenced by the ordering of the molecules [26–28]. This can be studied by measuring the selective reflection of light which occurs when its wavelength in the medium equals the pitch of this helix [1, 2]. To determine the influence of the different spacers on the selective reflection wavelengths of the planar oriented chiral nematic phase, the transmission spectra of compounds **III** were measured as a function of temperature (see figure 3). The reflection wavelengths of compound **III-4,4** 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 become important.

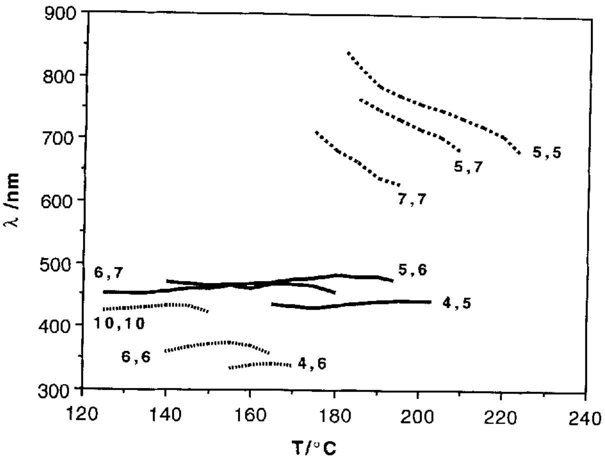


Figure 3. Dependence of the selective reflection wavelength on temperature for compounds **III**-n, m in the chiral nematic phase.

As can easily be seen, the results also fall into three groups. The compounds with odd–odd (n, m) reflect at a higher wavelength and this wavelength decreases with increasing temperature and spacer length. The reflection wavelengths of the compounds with even–even (n, m) are lower and increase with increasing spacer length. The reflection wavelengths for these compounds are almost insensitive to temperature. The compounds with odd–even (n, m) reflect around 450 nm, which is between the reflection wavelengths of the two other groups. There is no clear spacer length dependence for compounds in this group, but the reflection wavelength seems to increase slightly with temperature.

Although it is not possible to determine the reflection wavelengths of all the compounds at the same temperature, it is apparent that there is a strong odd-even effect for the reflection wavelengths of compounds with odd–odd and compounds with even–even (n, m). This odd–even effect attenuates with increasing spacer length and also with temperature. Here again the compounds with odd–even (n, m) have properties intermediate between those of the other two groups and effectively behave as a mixture of twins. As described previously, the selective reflection wavelengths of a mixture of chiral twin liquid crystalline cholesteryl ω-(4′-cyanobiphenyl-4-yloxy)alkanoate compounds with an odd and an even spacer are also intermediate between those of the pure compounds [25]. When the temperature dependences of the selective reflection wavelengths of the three groups of compounds are compared, the much stronger temperature dependence of the compounds with odd–odd (n, m) in their spacers is striking. It seems logical to propose that triplet liquid crystalline molecules with a more *trans*-like ordered structure with parallel directors of all three mesogenic units give rise to a smaller twist angle in the chiral nematic phase and therefore to a larger helical pitch and higher reflection wavelength than triplet compounds in which not all the directors of the mesogenic groups are parallel. Although the nematic phase favours an extended all-*trans*-conformation of alkyl chains, a certain fraction of bent rotamers is always present [21–23]. This fraction will of course increase with increasing chain length and also with increasing temperature. For our compounds with odd–odd (n, m), this leads to a disorder in the chiral nematic phase and therefore a decrease of the reflection wavelength. For the compounds with even–even (n, m), an increase of spacer length and temperature will lead to more *syn*-conformations and should lead to a slightly better ordered phase and therefore a higher reflection wavelength. The increase of the reflection wavelength with spacer length is clearly observed, and although the effect with temperature is small, this is also what is actually observed. Introduction of more *syn*-conformations in the compounds with odd–even (n, m) could lead to better or worse ordered phases, depending on the spacer in which the conformation changes take place. Due to this self-compensating effect, no strong influence of temperature or spacer length on the reflection wavelength of these compounds is expected. Figure 3 shows that these compounds exhibit broad chiral nematic ranges with no clear spacer length dependence and only a small temperature dependence.

4. Conclusions

For the first time a series of chiral triplet liquid crystals has been prepared and investigated. They show strong odd–even effects as a function of spacer length for the thermotropic and optical properties of their chiral nematic phases. The compounds with one odd and one even spacer show properties which are intermediate between those of compounds with two odd and compounds with two even spacers. The parallel orientation of the central aromatic group and one of the terminal dihydrocholesteryl moieties seems to be more important for the ordering of the chiral nematic phase than the parallel orientation of the terminal dihydrocholesteryl moieties. The compounds with one odd and one even spacer have broad range chiral nematic phases with a pitch which is almost temperature independent.

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