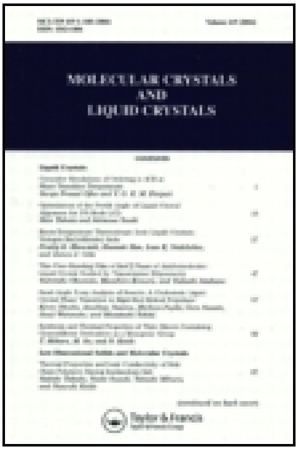


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Triplet Liquid Crystals Based on Isolithocholic Acid

Antonius T.M. Marcelis [a], Arie Koudijs [a] & Ernst J.R. Sudhölter [a]

[a] Laboratory for Organic Chemistry, Department of Biomolecular Sciences, Wageningen Agricultural University, Dreijenplein 8, 6703 HB, Wageningen, The Netherlands

Version of record first published: 24 Sep 2006

To cite this article: Antonius T.M. Marcelis, Arie Koudijs & Ernst J.R. Sudhölter (1999): Triplet Liquid Crystals Based on Isolithocholic Acid, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 330:1, 45-52

To link to this article: http://dx.doi.org/10.1080/10587259908025575

Mol. Cryst. Liq. Cryst., 1999, Vol. 330, pp. 45-52
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Triplet Liquid Crystals Based on Isolithocholic Acid

ANTONIUS T.M. MARCELIS, ARIE KOUDIJS
and ERNST J.R. SUDHÖLTER

*Laboratory for Organic Chemistry, Department of Biomolecular Sciences,
Wageningen Agricultural University, Dreijenplein 8, 6703 HB Wageningen,
The Netherlands*

Several triplet liquid crystals based on isolithocholic acid as central unit and cyanobiphenyl units as terminal mesogens have been prepared. The lengths of both spacers have been varied. The chiral nematic – isotropic transition temperatures and selective reflection wavelengths of the chiral nematic phases of the pure compounds and as guests in a liquid crystalline host show only weak odd – even effects as a function of the parity of the spacers. This is due to the fact that the bonds connecting the steroid nucleus with the spacers are not parallel with the long axis of the steroid, therefore changing the parity of the spacer does not result in a significant change in the ordering of the phases.

Keywords: trimer; cholesteric; selective reflection; odd – even effect; steroid

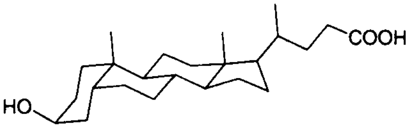
INTRODUCTION

Twin or dimer liquid crystals, containing two mesogenic moieties separated by a flexible spacer show strong odd - even effects as a function of the length and parity of the spacer[1]. These odd - even effects are manifested in the transitional properties like the isotropization temperatures and the corresponding enthalpy changes. Chiral twin liquid crystals with a cholesteric phase also show a strong odd - even effect in the selective reflection wavelength typical for the helix structure of the cholesteric phase[2-6]. Twin liquid crystals with an even number of flexible units like methylene, ether or carbonyl groups exhibit higher isotropization temperatures, stronger heat effects and have higher selective reflection wavelengths than the corresponding compounds with an odd number of flexible units in their spacer. It is assumed and also supported by measurements and calculations that the compounds with an even number of flexible units in their spacers are better ordered in the liquid crystalline phases, because the mesogenic units can more easily assume a parallel orientation[1].

Twin liquid crystals can be regarded as model compounds for main chain liquid crystalline polymers, where similar odd - even effects have been observed as a function of the length and the parity of the spacers. Triplet or trimer liquid crystals have also been regarded as model compounds for main chain liquid crystalline polymers[1,6,7]. Recently, we investigated triplet liquid crystals consisting of two cholestanyl moieties connected by flexible alkanoate spacers to a central biphenyl unit and found odd - even effects that were analogous to those found for the corresponding twins[8]. The odd - even effects were additive, *i.e.* compounds with two even spacers gave the best ordered phases with high isotropization temperatures, enthalpy changes and selective reflection wavelengths. Compounds with two odd spacers gave a poor ordering and those with one odd and one even spacer had intermediate properties.

Other series of triplet liquid crystals based on estradiol as central mesogen with cyanobiphenylyloxy groups as terminal mesogens also gave odd - even effects as a function of the spacer lengths[9,10]. However, the odd - even effect observed for the spacer at the 17-position of estradiol was reversed. This was explained by the fact that the bond connecting the central estradiol group with the spacer is not oriented parallel to the long axis of the rigid steroid moiety, but has a distinct angle with this axis. Therefore, the estradiol and the cyanobiphenyl group at the 17-position become better ordered with an odd spacer and less ordered with an even spacer. For the most often used aromatic mesogens and also for the 3-position of cholesterol or estradiol the bond connecting the mesogen with the spacer is parallel to the long axis of the rigid mesogen.

We decided to investigate further the effect of bond orientation on the mesogenic properties by studying a series of triplet compounds containing the bifunctional steroid isolithocholic acid as central unit and cyanobiphenylyloxy groups as terminal units. The main difference between the structure of isolithocholic acid and that of for example cholesterol is that the A and B rings are *cis*-connected, giving a kink in the overall structure (Figure 1). Furthermore, isolithocholic acid has a β-hydroxyl group at the 3-position. This was chosen to obtain a connecting group that is assumed to be better able to give a linear structure of the whole molecule.



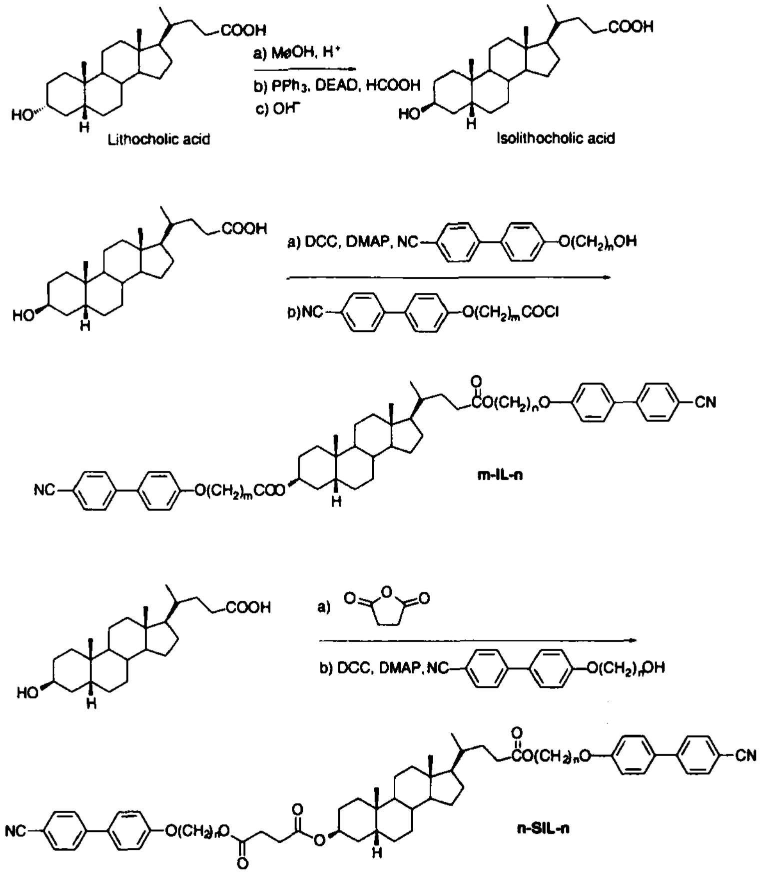
3 Isolithocholic acid

FIGURE 1 Structure of isolithocholic acid

In this paper the synthesis and properties of these molecules are described in order to evaluate the effect on the liquid crystalline behavior of the orientation of the bond connecting the central group with the flexible spacers.

RESULTS AND DISCUSSION

Two series of triplets were prepared. The synthesis of the compounds is illustrated in Scheme 1. First, isolithocholic acid was prepared from lithocholic acid by a three step procedure in which the essential step is a Mitsonobu reaction to convert the α-OH in a β-formate ester[11]. After hydrolysis of the ester groups isolithocholic acid is obtained. For the preparation of the **m-IL-n** compounds we first introduced the ester group at the carboxylic end of isolithocholic acid



SCHEME 1 Synthetic routes for the triplet liquid crystals

by a DCC induced coupling with the cyanobiphenylyloxy substituted alcohol. Under these conditions selective esterification was observed, because the primary OH function of this alcohol is more reactive than the secondary 3-OH group of isolithocholic acid. The ester group at the 3-position was introduced using the acid chloride of the appropriate cyanobiphenylyloxyalkanoic acid. For

TABLE I Thermotropic properties of the triplet liquid crystals as pure compounds and as a 5% guest in a cholesteric host*

Compound	Mpt (°C)	T(N*-I) (°C)	ΔH(N*-I) (J/g)	T(N*-I) (°C) in host	Δλ (nm) in host
5-IL-10	120	84	7	73.7	55
5-IL-11	115	85	6	76.4	46
5-IL-12	112	79	6	73.6	51
6-IL-10	119	70	7	75.6	7
6-IL-11	114	66	7	75.4	27
6-IL-12	106	71	7	76.2	5
10-SIL-10	74	53	6	75.1	25
11-SIL-11	91	67	9	75.9	38
12-SIL-12	81	61	7	75.5	19

* The host is a 1 : 2 mixture of cholesteryl chloride and cholesteryl nonanoate: λrefl = 640 nm and T(N*-I) = 77°C.

the **n-SIL-n** compounds isolithocholic acid was first reacted with succinic anhydride. The resulting bis-acid was esterified with a cyanobiphenylyloxy-alcohol using DCC as coupling agent. All compounds gave single spots on thin layer chromatography and NMR spectroscopy confirmed the purity and structure of the new compounds.

The liquid crystalline properties of the compounds as obtained by polarization microscopy and differential scanning calorimetry are collected in Table I. The properties have been determined of the pure compounds and also of mixtures containing the compounds as a 5% guest in a liquid crystalline host consisting of a 1 : 2 mixture of cholesteryl chloride and cholesteryl nonanoate[4,12].

All compounds are monotropic liquid crystals. This may be caused by the fact that although isolithocholic acid has a rigid elongated structure, it is not a good mesogen. For the **n-IL-m** compounds weak odd - even effects are observed for T(N*-I) within the series **5-IL-n** and **6-IL-n** both as pure compounds and in the guest - host mixtures. This is also shown in Figure 2

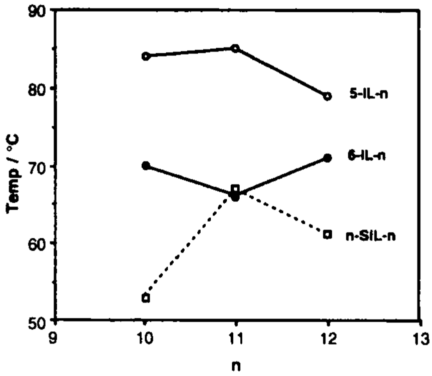


FIGURE 2 Temperatures T(N*-I) of the triplets as a function of n.

where T(N*-I) of the compounds is plotted against n. The weak odd - even effects are caused partially by the fact that the spacers are rather long, but also by the fact that the bonds connecting the central mesogen with the spacers are not parallel with the long axis of the molecule. It is also seen that the T(N*-I) of the **5-IL-n** compounds are slightly higher than of the **6-IL-n** compounds, suggesting a stronger odd - even effect for the spacer at the 3-position, because for m = 5 the spacer is even. The corresponding enthalpy changes are all in the same range and give no clue about an odd - even effect. The reversed dependence of T(N*-I) on n for the **5-IL-n** and **6-IL-n** series suggests that the total number of flexible units between the cyanobiphenyl units is important for the ordering. For the **n-SIL-n** compounds both spacers change when n is changed. When looking at the parity of both spacers it is better to compare **10-SIL-10** and **12-SIL-12** with **6-IL-10** and **6-IL-12** respectively, and **11-SIL-11** with **5-IL-11**. The effect of spacer parity on T(N*-I) is now comparable. The highest T(N*-I) are found for **11-SIL-11** and **5-IL-11**. This also suggests a stronger odd - even effect of the spacer at the 3-position.

The selective reflection wavelengths (λrefl) of the compounds were measured as pure compunds for **5-IL-n** and for all compounds as a mixture in the host. For the **6-IL-n** and **n-SIL-n** series λrefl was outside the visible

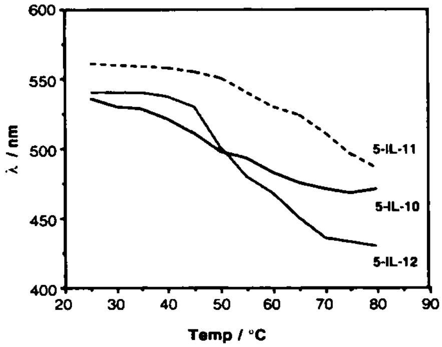


FIGURE 3 Selective reflection wavelengths (λrefl) of compounds **5-IL-n** as a function of temperature.

range or their measurement was hampered by slow crystallization. In Figure 3 the λrefl of the **5-IL-n** compounds is plotted as a function of temperature. It is seen that λrefl for **5-IL-11** is slightly larger than that for **5-IL-10** and **5-IL-12**. This points to a better ordering for this compound and agrees with the T(N*-I) measurements. In Table I the change in λrefl of the host (640 nm) is given when 5% guest is present. All compounds increase λrefl. This suggests that the screw sense of the helix of the guest is different from that of the host, which has a left-handed helix. This was confirmed by independent observations on pure **5-IL-n** compounds, and means that the isolithocholic triplets give a right-handed helix. For the **m-IL-n** compounds it can be seen that the better ordered phases give a lower change in λrefl. This means that the guest has a longer pitch of opposite screw sense than the host. These results agree with previous findings that better ordered phases give a higher λrefl and therefore have a longer pitch of the helix of the cholesteric phase[14,8]. For the **n-SIL-n** compounds the interpretation of the λrefl results is more difficult. However, when we compare the results of **11-SIL-11** with those of **5-IL-11** and those of **10-SIL-10** and **12-SIL-12** with those of **6-IL-10** and **6-IL-12**, the same trend in Δλ is found, namely Δλ of **5-IL-11** and **11-SIL-11** are higher than those of the other compounds.

Concluding, the triplet liquid crystals described in this paper give only weak odd - even effects in their isotropization temperatures and selective reflection wavelengths upon varying the parity of the spacers. This is probably due to the fact that the direction of the bonds connecting the steroid with the spacers is not parallel with the long axis of the steroid, which would give a "normal" strong odd - even effect, nor near 70°, wich is expected to give a "reversed" odd - even effect, but somewhere intermediate between these values. Molecular mechanics on isolithocholic acid also suggests intermediate angles. This means that upon changing the parity of the spacer the mutual ordering between the rigid units does not become much better or worse. Therefore no strong odd - even effects are observed for these compounds.

References

[1] G.R. Luckhurst, *Macromol. Symp.*, **96,** 1 (1995)

[2] A.T.M. Marcelis, A. Koudijs, and E.J.R. Sudhölter, *Recl. Trav. Chim. Pays-Bas,* **113,** 524 (1994)

[3] A.T.M. Marcelis, A. Koudijs, and E.J.R. Sudhölter, *Liq. Cryst.,* **18,** 843 (1995)

[4] A.T.M. Marcelis, A. Koudijs, and E.J.R. Sudhölter, *J. Mater. Chem.,* **6,** 1469 (1996)

[5] A.E. Blatch, I.D. Fletcher, and G.R. Luckhurst, *J. Mater. Chem.,* **7,** 9, (1997)

[6] N.V. Tsvetkov, V.V. Zuev, and V.N. Tsvetkov, *Liq. Cryst.,* **22,** 245 (1997)

[7] C.T. Imrie, and G.R. Luckhurst, *J. Mater. Chem.,* **8,** 1339 (1998)

[8] A.T.M. Marcelis, A. Koudijs, and E.J.R. Sudhölter, *Liq. Cryst.,* **18,** 851 (1995)

[9] A.T.M. Marcelis, A. Koudijs, and E.J.R. Sudhölter, *Liq. Cryst.,* **21,** 87 (1996)

[10] A.T.M. Marcelis, A. Koudijs, and E.J.R. Sudhölter, *Thin Solid Films,* **284–285,** 308 (1996)

[11] A.K. Batta, S.K. Aggarwal, G. Salen, and S. Shefer, *J. Lipid Res.,* **32,** 977 (1991)

[12] T.D. James, H. Kawabata, R. Ludwig, K. Murata, and S. Shinkai, *Tetrahedron,* **51,** 555 (1995)