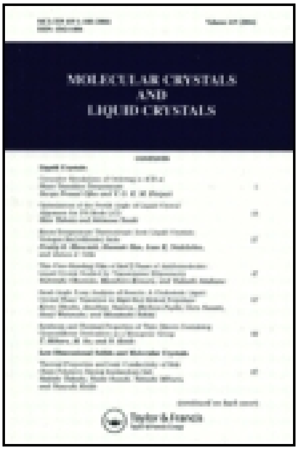


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

# Liquid Crystallinity of Non-Symmetrical Dimeric Compounds (I) Synthesis of 4-(4′-Benzyloxy)Biphenyl Cholesteryl Alkanedioates and their Phase Transition Behavior

Tomonori Hanasaki [a] [b] , Junko Kawashima [a] , Namiko Morishita [a] & Takuro Yamamoto [a]

[a] Department of Materials Science, Shizuoka Institute of Science and Technology, 2200-2 Toyosawa, Fukuroi, Shizuoka, 437-8555, Japan

[b] Department of Applied Chemistry, Faculty of Science and Engineering, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, Shiga, 525-8577, Japan

To cite this article: Tomonori Hanasaki, Junko Kawashima, Namiko Morishita & Takuro Yamamoto (2001): Liquid Crystallinity of Non-Symmetrical Dimeric Compounds (I) Synthesis of 4-(4′-Benzyloxy)Biphenyl Cholesteryl Alkanedioates and their Phase Transition Behavior, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 15-22

*Mol. Cryst. and Liq. Cryst.*, 2001, Vol. 365, pp. 15-22
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint,
a member of the Taylor & Francis Group,
Printed in the USA

# Liquid Crystallinity of Non-Symmetrical Dimeric Compounds (I) Synthesis of 4-(4'-Benzyloxy)Biphenyl Cholesteryl Alkanedioates and their Phase Transition Behavior

TOMONORI HANASAKI*, JUNKO KAWASHIMA,
NAMIKO MORISHITA and TAKURO YAMAMOTO

*Department of Materials Science, Shizuoka Institute of Science and Technology,*
*2200–2 Toyosawa, Fukuroi, Shizuoka 437–8555, Japan*

A new series of non-symmetrical dimeric compounds containing two distinct mesogenic groups, 4-(4'-benzyloxy)biphenyl cholesteryl alkanedioates, was prepared in our laboratory. In addition, two symmetrical dimers, dichoresteryl decanedioate and di[4-(4'-benzyloxy)biphenyl] decanedioate, were synthesized. The phase transition behavior of these compounds has been studied by a differential scanning calorimeter and a polarizing microscope. In the case of the symmetrical dimers, dichoresteryl decanedioate gave rise to a monotropic cholesteric phase and di[4-(4'-benzyloxy)biphenyl] decanedioate showed no liquid crystallinity. On the other hand, 4-(4'-benzyloxy)biphenyl cholesteryl decanedioate which is the non-symmetrical dimer gave rise to three liquid crystalline phases in wide temperature range. Moreover, a typical even-odd effect with regarded to the phase transition behavior was observed for the non-symmetrical dimeric compounds.

*Keywords:* non-symmetrical dimer; liquid crystal; even-odd effect

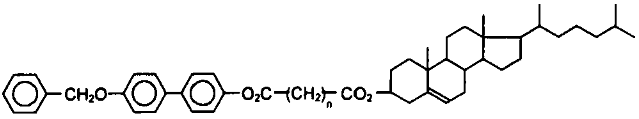
---

* Corresponding author. Present address: Department of Applied Chemistry, Faculty of Science and Engineering, Ritsumeikan University, 1–1–1 Nojihigashi, Kusatsu, Shiga 525–8577, Japan.

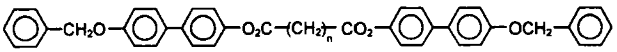
## INTRODUCTION

Many liquid crystalline dimeric compounds, in which two mesogenic groups are linked by a flexible spacer, have been synthesized and their phase transition behavior has been investigated[1,2]. These liquid crystalline dimers are expected to be a model compound for main chain liquid crystalline polymers[1] and to exhibit different properties to other conventional low molar mass liquid crystals[2]. Most of liquid crystalline dimers synthesized hitherto are symmetrical ones of which molecules have two same mesogenic groups. However, non-symmetrical dimeric compounds of which molecules have two distinct mesogenic groups are also interesting materials, because it is possible to imagine the various combinations of the mesogenic groups such as a chiral mesogenic group and a non-chiral one, a positive dielectric property and a negative one, and so on. Therefore, these non-symmetrical dimers are expected to exhibit unique properties different from those of the symmetrical dimers. However, there are not many reports about such dimers[3].

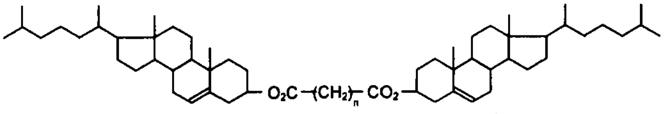
In the present study, novel non-symmetrical dimeric compounds were synthesized. The compounds designed here were 4-(4'-benzyloxy) biphenyl cholesteryl alkanedioates. These molecules were constructed with two mesogenic groups, a cholesteryl and a 4-(4'-benzyloxy) biphenyl ones, and a flexible methylene chain. These compounds are abbreviated hereafter to BBChA-*n*, where *n* is the number of carbon atoms in the methylene chain unit. In addition, the symmetrical dimeric compounds, di[4-(4'-benzyloxy)biphenyl] alkanedioate (abbreviated hereafter to diBBA-*n*) and dichoresteryl alkanedioate (abbreviated hereafter to diChA-*n*), were prepared. The phase transition behavior of diChA-*n* had been already reported by some groups[4]. However, the compound was freshly prepared in our laboratory in order to discuss the phase transition behavior under the same conditions as BBChA-*n* and diBBA-*n*. General structures of objective compounds are shown in below. The phase transition behavior of these compounds was studied using a polarizing microscope and a differential scanning calorimeter.



BBChA-*n* (*n*=2-8 and 10)



diBBA-*n* (*n*=8)



diChA-*n* (*n*=8)

## EXPERIMENTAL

The non-symmetrical dimers, BBChA-*n*, were synthesized by the routes illustrated in Figure 1. The purification of the products was made by a column chromatography (silica gel, ethyl acetate-hexane) and a recrystallization (ethyl acetate-methanol). The synthetic procedures of diBBA-8 were similar to those of the step (1) and (2) in the case of BBChA-8 except for the molar ratio of the starting materials in the step (2) (**c**/**d**/pyridine 2.4/1.0/2.8). The product was purified by the column chromatography (silica gel, dichloromethane) and the recrystallization (ethyl acetate). On the other hand, diChA-8 was prepared from cholesterol and 1,10-decanedioic acid by an esterification in benzene containing a catalytic amount of *p*-toluenesulfonic acid. The purification of the compound was made by the recrystallization (chloroform-methanol). $^1$H-NMR (JEOL, JNM EX-400) spectra were used for an identification of the synthesized compounds. The purity of the compounds was confirmed by a presence of only one spot through the TLC analyses in addition to the results of the $^1$H-NMR spectra in which no other peaks were observed except for the identified peaks as the objective compounds.

The thermal measurements were made by the differential scanning calorimeter (Perkin Elmer Pyris 1, abbreviated hereafter to DSC) and the scanning rate was 5.0℃/min. The texture observations were carried out using the polarizing microscope (Nikon X2TP-11) equipped with a heating stage (LINKAM-600PM). The scanning rate was 5.0℃/min in analogy with DSC measurements.

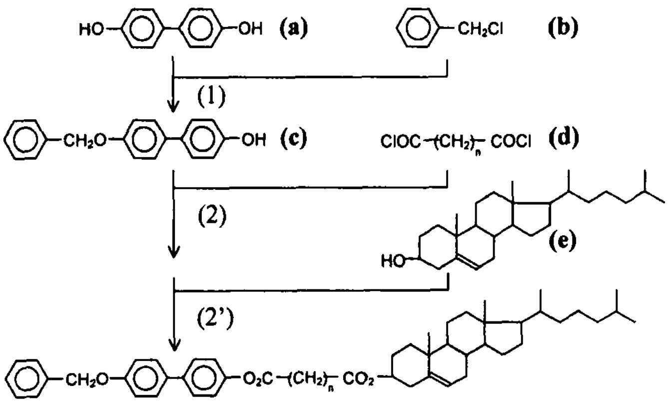


FIGURE 1 Scheme of synthetic process. (1)**a**/**b**/NaOH (initial molar ratio1.0/1.2/0.7, methanol (reflux 24h), yield 70%. (2)**c**/**d**/pyridine (1.2/1.0/1.4), methylene chloride (reflux 24h). (2')immediately after the procedure (2), **e**/pyridine (1.2/1.4), (reflux 24h), yield 59%(*n*=7).

## RESULTS AND DISCUSSION

From the results of the thermal measurements and the texture observations, the phase transition behavior of BBChA-*n* (*n*=2-8 and 10), diBBA-8, and diChA-8 after the 1st cooling is summarized in Table 1. Although a crystal-crystal phase transition behavior was observed in some compounds, the characterization of each crystal phase was not carried by an appropriate method such as an X-ray diffraction one. Therefore, such behavior was not noted in Table 1 and no discussion was held in this paper.

The symmetrical dimeric compounds, diBBA-8 showed no liquid crystallinity. This result may be due to the structure of the mesogenic group containing a benzyl ether unit. The shape of the mesogenic group is not linear because of this ether unit, and this shape is a disadvantage to form the liquid crystalline phase. Only monotropic phase was observed for diChA-8 as already reported by other researchers[4]. In contrast with these results, BBChA-8 which was non-symmetrical dimer exhibited two enantiotropic and one monotropic liquid crystalline phases. One of the enantiotropic phases observed in highest temperature region was identified as a cholesteric (Ch) phase, because a typical fan-shaped texture was observed under the polarizing microscope and this texture was changed into a planar one by a slip of the cover glass on the sample. The microscopic texture of the second enantiotropic liquid crystalline phase was a typical focal conic texture, and that of the monotropic phase was a schlieren one. It is considered that the second enantiotropic phase is a smectic A ($S_A$) and the monotropic phase is smectic C ($S_C$) from the results of the microscopy observations. However, experiments using the X-ray diffraction methods are required

TABLE 1 Phase transition temperatures.

| sample | phase transition temperatures ／ ℃ |
|---|---|
| BBChA-2 | $\mathrm{K} \xrightarrow{173} \mathrm{Ch} \xrightarrow{240} \mathrm{I.L.}$<br>$\mathrm{K} \xleftarrow[151]{} \mathrm{Ch} \xleftarrow[238]{} \mathrm{I.L.}$ |
| BBChA-3 | $\mathrm{K} \xrightarrow{145} \mathrm{Ch} \xrightarrow{165} \mathrm{I.L.}$<br>$\mathrm{K} \xleftarrow[130]{} \mathrm{Ch} \xleftarrow[164]{} \mathrm{I.L.}$ |
| BBChA-4 | $\mathrm{K} \xrightarrow{135} \mathrm{S_A} \xrightarrow{160^*} \mathrm{Ch} \xrightarrow{219} \mathrm{I.L.}$<br>$\mathrm{K} \xleftarrow[96]{} \mathrm{S_C} \xleftarrow[125]{} \mathrm{S_A} \xleftarrow[165^*]{} \mathrm{Ch} \xleftarrow[219]{} \mathrm{I.L.}$ |
| BBChA-5 | $\mathrm{K} \xrightarrow{137} \mathrm{Ch} \xrightarrow{163} \mathrm{I.L.}$<br>$\mathrm{K} \xleftarrow[117]{} \mathrm{Ch} \xleftarrow[164]{} \mathrm{I.L.}$ |
| BBChA-6 | $\mathrm{K} \xrightarrow{118} \mathrm{S_A} \xrightarrow{160} \mathrm{Ch} \xrightarrow{193} \mathrm{I.L.}$<br>$\mathrm{K} \xleftarrow[80]{} \mathrm{S_C} \xleftarrow[85]{} \mathrm{S_A} \xleftarrow[158^*]{} \mathrm{Ch} \xleftarrow[193]{} \mathrm{I.L.}$ |
| BBChA-7 | $\mathrm{K} \xrightarrow{122} \mathrm{Ch} \xrightarrow{158} \mathrm{I.L.}$<br>$\mathrm{K} \xleftarrow[91]{} \mathrm{Ch} \xleftarrow[158]{} \mathrm{I.L.}$ |
| BBChA-8 | $\mathrm{K} \xrightarrow{121} \mathrm{S_A} \xrightarrow{148} \mathrm{Ch} \xrightarrow{177} \mathrm{I.L.}$<br>$\mathrm{K} \xleftarrow[78]{} \mathrm{S_C} \xleftarrow[90]{} \mathrm{S_A} \xleftarrow[143^*]{} \mathrm{Ch} \xleftarrow[177]{} \mathrm{I.L.}$ |
| BBChA-10 | $\mathrm{K} \xrightarrow{105} \mathrm{S_A} \xrightarrow{143} \mathrm{Ch} \xrightarrow{166} \mathrm{I.L.}$<br>$\mathrm{K} \xleftarrow[80]{} \mathrm{S_C} \xleftarrow[100^*]{} \mathrm{S_A} \xleftarrow[138]{} \mathrm{Ch} \xleftarrow[165]{} \mathrm{I.L.}$ |
| diBBA-8 | $\mathrm{K} \xrightarrow{209} \mathrm{I.L.}$<br>$\mathrm{K} \xleftarrow[200]{} \mathrm{I.L.}$ |
| diChA-8 | $\mathrm{K} \xrightarrow{180} \mathrm{I.L.}$<br>$\mathrm{K} \xleftarrow[158]{} \mathrm{Ch} \xleftarrow[180]{} \mathrm{I.L.}$ |

K : crystal, Ch : cholesteric phase

$\mathrm{S_A}$ : smectic A phase $\mathrm{S_C}$ : smectic C phase

I.L.: isotropic liquid

* : The temperature was decided by microscopy observations.

The types of the liquid crystalline phases were decided by microscopy observations.

to make sure of these smectic types. These experiments are now in progress. The results obtained for BBChA-8, diBBA-8, and diChA-8 suggest that the coexistence of two distinct mesogenic groups in one molecule cause to stabilize the liquid crystalline phases and to induce the smectic phases. From the results, it can be considered that a supplemental relationship exists between the two mesogenic groups, that is, one mesogenic group is act as a support group to form the liquid crystalline phase by the other mesogenic group. The DSC results for BBChA-8 showed one remarkable feature. An exothermic peak corresponding to Ch-$S_A$ transition in the cooling process was not clearly detected, and an endothermic peak corresponding to $S_A$-Ch transition in the heating process was very broad. This fact showed that this phase transition needs a relatively long time. One of the possible reasons may be also the effect of the coexistence of the two distinct mesogenic groups. It is considered that one mesogenic group remained an initial state whereas the other mesogenic group started to change to the next liquid crystalline phase. Consequently, the phase transition may become to be a time-consuming process.

As can be seen from Table 1, the even carbon number series of BBChA-*n* except for BBChA-2 gave rise to three liquid crystalline phases. The remaining sample, odd carbon number series and BBChA-2 which has shortest methylene chain in the even members, showed only enantiotropic Ch phase. These results are explained as follows. When the methylene chain has even carbon atoms and all of them adapt a *trans* conformation, the molecule is regarded as rod-like because the two mesogenic groups which are bulky ones lie in *trans* positions to each other. Therefore, the layer structure such as the smectic one can be easily formed. On the other hand, in the odd members, the molecules are difficult to form the layer structure because the two mesogenic groups lie in *cis* position to each other and the shape of the molecules may be far from rod-like[5]. In the case of BBChA-2, even if the two mesogenic groups lie in the *trans* positions to each other, it is difficult to regard the shape of the molecule as rod-like owing to the short flexible chain. Consequently, the same result was obtained as those of the odd members. This structural difference between the even and the odd members may affect their phase transition temperatures. As can be seen from Table 1, the clearing temperatures of the even members are higher than those of the odd members, and the liquid crystalline temperature ranges of the even members are wide in contrast to those of the odd members.

In order to discuss the behavior of two distinct mesogenic groups at the phase transition point and the even-odd effect with regarded to the phase transition behavior in detail, the syntheses of BBChA-*n* which has the longer methylene chain are now in progress.

## References

[1] For example, Y. Ogawa and K. Takamizawa, *Polymer J.*, **21**, 551 (1989).

[2] For example, A. Yoshizawa and I. Nishiyama, *J. Mater. Chem.*, **4**, 449 (1994).

[3] For example, G.S. Attard, R.W. Date, C.T. Imrie, G.R. Luckhurst, S.J. Roskilly, J.M. Seddon, and L. Taylor, *Liq. Cryst.*, **16**, 529 (1994).

[4] For example, A.T.M. Marcelis, A. Koujdijs, and E.J.R. Sudholter, *J. Mater. Chem.*, **6**, 1469 (1996).

[5] N. Nakamura, T. Hanasaki, and H. Onoi, *Mol. Cryst. Liq. Cryst.*, **225**, 269 (1993).