Host–guest effect on chirality transfer from a binaphthyl derivative to a host nematic liquid crystal†

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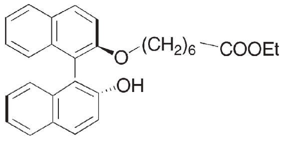
A novel dichiral compound possessing both an asymmetric axis and a chiral centre induces opposite twist senses and distinct helical pitches in different host nematic liquid crystals; the host–guest effect on chirality transfer is discussed in terms of molecular recognition.

Chiral information transfer has been of great interest in various fields of materials science.[1–3] Investigation of chirality in liquid crystals is an exciting area of liquid crystal science.[4] Chirality-dependent frustrated phases, *i.e.* twist grain boundary phases and blue phases, have been investigated.[5] The appearance of these phases is created by the competition between chiral twisting force and the molecules' packing such that they fill the space uniformly. Ferroelectricity has been observed in chiral tilted smectic phases.[6] The introduction of chirality into calamitic molecules engenders a reduction in the symmetry of the classical smectic C phase and causes the helical structure characteristic of the chiral smectic C phase, which can induce ferroelectricity. The question of how molecular chirality is translated into bulk chirality of the liquid crystalline phase is a fundamental issue in liquid crystal science. A macroscopic measure of this chirality transfer is the helical pitch or helical twisting power (HTP). It has been possible to identify several qualitative correlations between the structure of mesogenic chiral molecules and the pitch of their corresponding chiral nematic phases.[7–10] Chiral induction behaviour of molecules with atropisomeric biphenyl cores in ferroelectric liquid crystals was explained by chiral molecular recognition that a favourable structural match exists between chiral dopant and host molecules to undergo chirality transfer *via* core–core interactions.[11] Intra-molecular and inter-molecular chirality transfer processes have been investigated in systems of atropisomers as chiral dopants.[12] Recently, Kaszynski *et al.* reported that lower conformational freedom and higher structural rigidity of both a chiral additive and a host engender higher HTP values.[13] On the other hand, theoretical studies show that short-range biaxial correlations play a central role in determining the chiral nematic pitch.[14] A molecular theory of helical twist inversion in chiral nematic liquid crystals was reported by Emelyanenko *et al.*, who noted that biaxiality of a chiral dopant molecule appears to be an important factor that strongly affects the value and sign of HTP.[15]

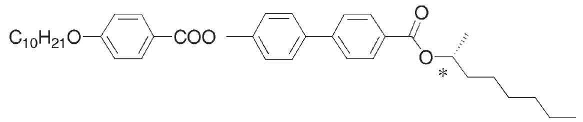
We investigated a homologous series of dimeric liquid-crystalline compounds possessing a binaphthyl group and found an unusual phase sequence of iso liq–blue phase–smectic A.[16] In this report, we describe the design of a novel dichiral compound that possesses both an asymmetric axis and an asymmetric centre; we further investigate the induced helical structure in a host nematic liquid crystal.

The dichiral compound, (*R*,*R*)-4-[4-(1-methylheptyloxycarbonyl)phenyl]phenyl 7-[(1,1′-binaphthalene)-2-hydroxy-2′-yloxy]heptanoate **(*R*,*R*)-BM**, was prepared by the synthesis outlined in Scheme 1 (see also ESI†). 4-Methoxycarbonyloxybiphenyl-4′-carboxylic acid was treated with (*S*)-2-octanol in the presence of PPh_3 and DEAD, and the protective group of the compound was removed by aminolysis to give (*R*)-1-methylheptyl 4-hydroxybiphenyl-4′-carboxylate. Then, (*R*)-1,1′-bi(2-naphthol) was treated with ethyl 7-bromoheptanoate in the presence of potassium carbonate; the obtained ester was hydrolyzed to give the corresponding carboxylic acid. The intermediate was treated with (*R*)-1-methylheptyl 4-hydroxybiphenyl-4′-carboxylate in the presence of DCC to give the target compound, **(*R*,*R*)-BM**, as a colourless liquid. Its purity was determined to be 100% using HPLC analysis. The structure was elucidated using IR and ^{1}H NMR.

For comparison, the corresponding monochiral compounds, **(*R*)-B** with an asymmetric axis and **(*R*)-M** (10B1M7[17]) with an asymmetric carbon, were also prepared.



(*R*)-B



(*R*)-M

On cooling, **(*R*,*R*)-BM** exhibited a glass transition at 14 °C. We investigated the helical sign and pitch induced by each chiral dopant in different host nematic compounds. Two host liquid-crystalline compounds were used: 5-heptyl-2-(4-hexyloxyphenyl)-pyrimidine **(7-PYP-6O)** and 4-hexyloxy-4′-cyanobiphenyl **(6OCB)**. The helical pitch in the N* phase was measured by the Cano wedge technique for a chiral nematic mixture consisting of a host nematic liquid-crystalline material and each chiral additive. The mixtures were studied using the contact method; their chiral nematic helical twist senses were established. The standard

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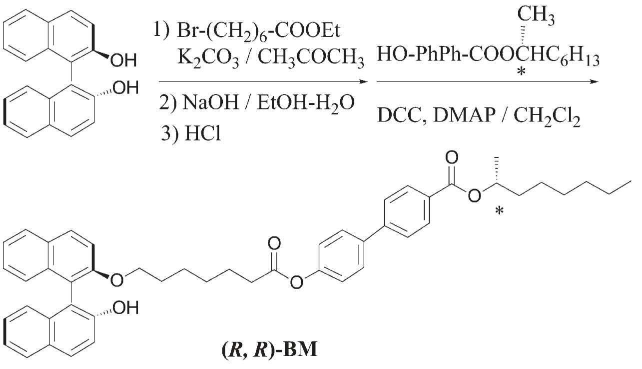

Scheme 1 Synthesis of ***(R,R)*****-BM**.

materials used in the contact study were (*R*)-3-methyladipic acid bis[4-(5-octyl-2-pyrimidinyl)phenyl]ester[18] and (*S*)-2-methylbutyl 4-(4-decyloxybenzylideneamino)cinnamate (DOBAMBC[19]). The definition of the helical twist senses used in this report is the same as that of Goodby.[20]

Fig. 1 shows the temperature dependence of helical pitch values induced by **(*R*)-M** or **(*R*)-B** in the mixture with 1 mol% of each host material. **(*R*)-M** was found to induce a left-handed (LH)-helical structure in each host. However, **(*R*)-B** was found to induce a right-handed (RH)-helical structure. The helical structure induced by each monochiral compound does not depend on the host structure. Fig. 2 shows the temperature dependence of helical pitch values induced by 2 wt% of **(*R*,*R*)-BM** in each host material.

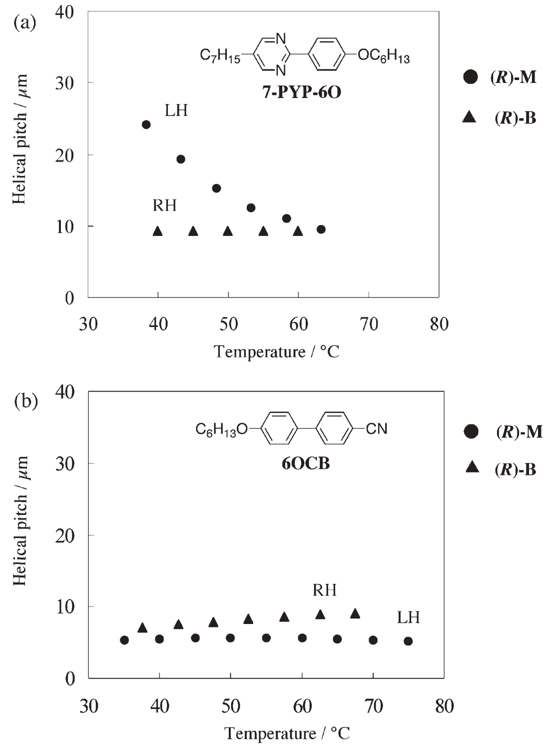

Fig. 1 Temperature dependence of helical pitch values induced by **(*R*)-M** or **(*R*)-B** in the mixture with **7-PYP-6O** (a) and that with **6OCB** (b). A chiral mixture consists of 1 mol% of each chiral additive and a host material. Transition temperatures (°C) of the host materials: **7-PYP-6O**, iso liq 68.0 N 36.5 recryst. mp 47.0; **6OCB**, iso liq 75.5 N 36.1 recryst. mp 56.1.

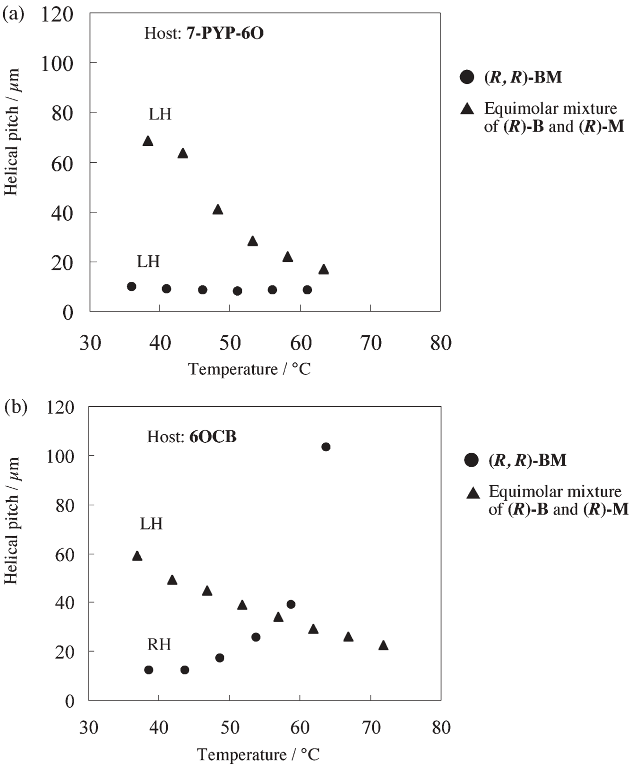

Fig. 2 Temperature dependence of helical pitch values induced by **(*R*,*R*)-BM** or an equimolar mixture of **(*R*)-M** and **(*R*)-B** in the mixture with **7-PYP-6O** (a), and that with **6OCB** (b). A chiral mixture consists of 2 wt% of each chiral additive and a host material.

For comparison, helical pitch values induced by an equimolar mixture of **(*R*)-B** and **(*R*)-M** in each host are also shown in Fig. 2.

In the mixture with **7-PYP-6O**, **(*R*,*R*)-BM** was found to induce a short helical pitch with the sense of LH. In the mixture with **6OCB**, **(*R*,*R*)-BM** induced a RH-helical structure and the pitch values became shorter with decreasing temperature. The helical sense and temperature dependence of the induced pitch are different for **(*R*,*R*)-BM** in different host liquid crystals. The equimolar mixture was found to induce an identical LH-helical structure and the pitch values became longer with decreasing temperature in each host material, indicating that twist interactions organized by **(*R*)-M** have a dominant contribution for the helical induction in each host and that the interactions are compensated with those of the opposite sign organized by **(*R*)-B** with decreasing temperature. Interestingly, marked differences exist in an induced helical structure between **(*R*,*R*)-BM** and the equimolar mixture. The results thus obtained reveal that the helical structure induced by **(*R*,*R*)-BM** in **7-PYP-6O** reflects chirality of the asymmetric carbon. However, that in **6OCB** reflects chirality of the asymmetric axis.

The chiral transfer from the dichiral compound to a host liquid crystal is interesting. An optically pure 2,2′-substituted 1,1′-binaphthyl molecule can exist in two conformations: either cisoid or transoid. The MM2 calculations of **(*R*,*R*)-BM** suggest that the cisoid conformation is more stable than the transoid: the energy difference was estimated to be 2 kJ mol^{-1}. Although the difference is not large, we assumed the cisoid conformer for **(*R*,*R*)-BM**. Fig. 3 shows possible models for interactions between the

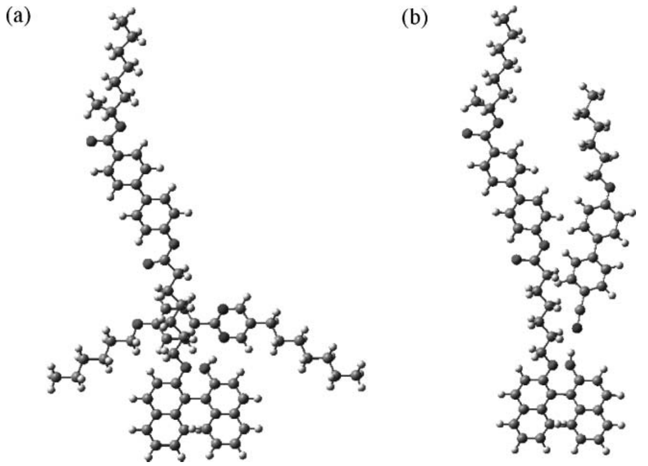

Fig. 3 A possible model using a Gaussian model for a twist interaction of ***(R,R)*-BM** with **7-PYP-6O** (a) and that with **6OCB** (b).

dichiral molecule and each host molecule. A twist interaction between the binaphthyl group and a host molecule is assumed to be organized by the core–core interaction.[21] That between the mesogenic group with an asymmetric carbon and a host molecule is assumed to be organized by biaxial correlations between each short axis.[14] We infer that the OH group can bind a host molecule *via* hydrogen bonding. Binding between monochiral compound ***(R)*-B** and each host molecule is also thought to occur in the mixture. However, the chiral information transfer from ***(R)*-B** to the host molecule does not depend on the host structure (see Fig. 1). The pyrimidine unit of **7-PYP-6O** is thought to interact with the OH group *via* hydrogen bonding, as shown in Fig. 3(a); consequently, the rotation of **7-PYP-6O** around its long axis might be restricted. As a result, the short-range biaxial correlations between the **7-PYP-6O** and the rod-like mesogenic part possessing an asymmetric carbon in the ***(R,R)*-BM** might strengthen. Therefore, chiral information of the asymmetric centre can be transferred to the host nematic molecule. On the other hand, **6OCB** is inferred to interact with ***(R,R)*-BM** *via* hydrogen bonding between CN and OH, as shown in Fig. 3(b). In that case, the rotation of **6OCB** around its long axis might not be hindered, and the relative configuration between **6OCB** and the rod-like mesogenic part of ***(R,R)*-BM** can be nearly parallel. The biaxial correlations between **6OCB** and the chiral mesogenic part should be weak. The twist core–core interaction between the binaphthyl group of ***(R,R)*-BM** and the biphenyl group of **6OCB** might have a dominant contribution for induction of the helical structure. In order to confirm the binding model, we have performed the control experiment of methylating the OH group of ***(R,R)*-BM**. The methylated compound was found to induce a LH-helical structure in each host material as same as the equimolar mixture (see Fig. S1 in the ESI†). The results clearly support the binding model.

In summary, dichiral compound ***(R,R)*-BM** was found to induce different helical structures, *i.e.*, opposite twist senses and distinct temperature dependence of helical pitch, in two host nematic liquid crystals, **7-PYP-6O** and **6OCB**. On the other hand, an equimolar mixture of the corresponding monochiral compounds, ***(R)*-B** and ***(R)*-M**, induced almost identical helical structures in the different hosts. The specific twist interaction of the dichiral compound with a host substance is explainable in terms of molecular recognition: that the 2-hydroxy-1,1′-binaphthyl unit acts as a binding site for a host molecule. The pseudo-intra-molecular chirality transfer from the chiral centre to the host molecule occurs *via* the short-range biaxial correlations. The host dependence for induction of the helical structure is attributed to the difference in the binding configuration. The present approach is an example of an enzyme-mimic design for an optically active additive in a mesophase system; it can suggest new aspects of chiral liquid crystals.

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