P-01

Synthesis and Helical Twisting Power of (*R*)-6,6'-Harogenated and -Methylated Binaphthyl Type Chiral Dopants

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Abstract

We synthesised (*R*)-6,6'-halogenated and -methylated binaphthyl derivatives to create chiral nematic liquid crystals (N*LCs) by doping them into two types of host nematic liquid crystals (NLCs) such as fluorinated and azomethyne type NLCs. The influence of substituent properties of the synthesised chiral dopants, steric, polarity and polarizability, on the helical twisting power (HTP) and their temperature dependence of HTP ($HTP_{t.d.}$) were investigated in the two above-mentioned NLCs. Our understating suggested that the chiral dopant bearing less steric and larger polarizability properties, *i.e.* the 6,6'-chlorinated chiral dopant, possessed the considerable large HTP value. Besides, the $HTP_{t.d.}$ values of the chiral dopants were affected by their substituents.

1. Introduction

The lack of mirror symmetry, referred to as chirality, has a remarkable influence on the microscopic physical properties of materials. Especially the chiral liquid crystals (CLCs), chiral nematic liquid crystals (N*LCs) and blue phase liquid crystals (BPLCs), exhibit unusual physical properties such as selective reflections in a visible wave length region. [1] The CLCs have potential applications in low energy consumption reflective liquid crystal displays because of their optical properties. [2] The development of CLCs or chiral dopants which enable to form N*LCs from achiral nematic liquid crystals (NLCs) has, therefore, attracted considerable attention.

Chiral dopants are asymmetric compounds possessing chirality such as central, axial, planer and helical chirality. The ability of chiral dopants to form N*LCs from host NLCs is evaluated by helical twisting power (HTP) expressed as below,

$$HTP = (P \times c_w)^{-1}$$

where HTP is helical twisting power (μm^{-1}), *P* is helical pitch of the chiral nematic phase and c_w is weight percent concentration of the chiral dopant [wt%].

We synthesised the 6,6'-fluorinated binaphthyl-type chiral dopant **(1b)** possessing a large HTP value, meaning good chirality transfer from a chiral dopant to host NLC, in the fluorinated host NLC as reported previously. [3] However, a chirality transfer mechanism between the chiral dopant and host NLC has not been well understood. Much progress and advancement would has been made in the liquid crystal science and technology, if the mechanism was to be understood.

In this study, we synthesised 6,6'-non substituted (**1a**), -halogenated (**1b-1e**) and -methylated (**1f**) binaphthy-type chiral dopants and examined dominant molecular factors like size, polarity and polarizability of their substituents affecting the induced absolute HTP (|HTP|) and their temperature dependence.

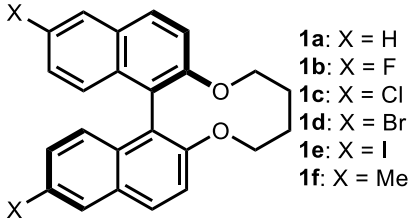

Figure 1. The chemical structures of synthesised chiral dopants.

2. Results and Discussion

2.1. Effect of substituents on the induced |HTP| value

The |HTP| values of **1a–f** in fluorinated (JC-1041XX) and azomethyne type (MBBA) NLCs are plotted for steric parameter (V_{vdw}) in Fig. 2 to exhibit a relationship between the steric effect of their substituents and their |HTP| values.

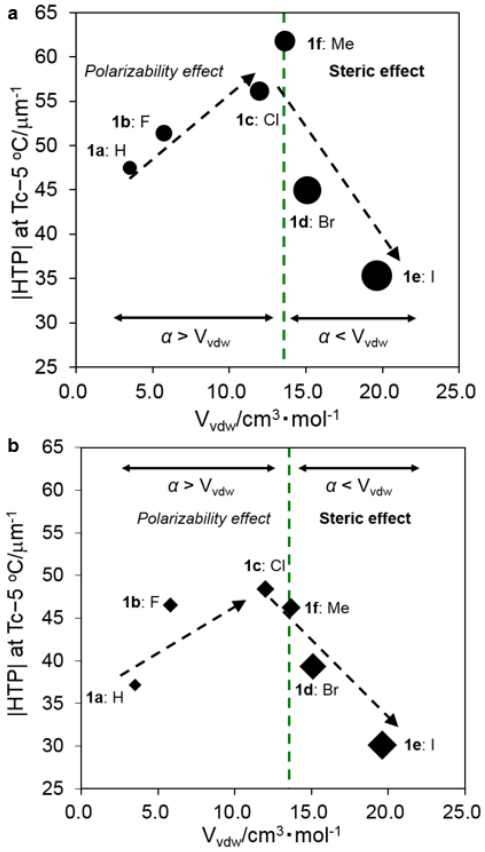

Figure 2. Plots of the |HTP| values of **1a-f** in (a) JC-1041XX and (b) MBBA vs. the V_{vdw} of their substituents.

The chiral dopant possessing less steric and larger polarizability, *i.e.* the 6,6'-chlorinated and -methylated bridged binaphthyl chiral dopant, tended to increase the |HTP| value in two different host NLCs, since the induce N*LC phase is composed of arene-arene interactions, affecting steric hindrance and polarizability between chiral dopants and NLC molecules.

2.2. Effect of substituents on the temperature dependence of HTP value

The temperature dependence of HTP ($HTP_{t.d.}$) value was defined as below,

$$HTP_{t.d.} = (\Delta HTP / \overline{HTP}) / \Delta T \times 100$$

where ΔHTP is the difference between the maximum and minimum |HTP| values, and $\overline{HTP}$ is the arithmetic mean of the |HTP| values in the temperature range from $T - T_c = -5$ to 25°C. [3] The $HTP_{t.d.}$ values of **1a-1f** were 0.46 (-H), 0.43 (-F), 0.59 (-Cl), 0.60 (-Br), 0.69 (-I) and 0.64 (-Me) $\%\cdot T^{-1}$ in JC-1041XX, respectively. By contrast, those of **1a-1f** were 0.49 (-H), 0.73 (-F), 0.85 (-Cl), 0.87 (-Br), 0.87 (-I) and 0.82 (-Me) $\%\cdot T^{-1}$ in MBBA. These values in two host nematics exhibited to correlate with steric and polarizability substituent parameters (JC-1041XX: the $HTP_{t.d.}$ values vs. steric parameter; $R^2 = 0.91$ and vs. polarizability parameters; $R^2 = 0.83$. MBBA: the $HTP_{t.d.}$ values vs. steric parameter; $R^2 = 0.73$ and vs. polarizability parameters; $R^2 = 0.54$.). Arene-arene interactions involving polarizability can impact the $HTP_{t.d.}$ values of the smaller substituents (-H < V_{vdw} < -Cl) of synthesised chiral dopants because these $HTP_{t.d.}$ values gradually increase as their polarizability increased. Moreover, the chiral dopants possessing a larger substituent (-Br and -I) should promote a disaggregation of the arene-arene interactions between these chiral dopants and the host NLC molecules.

3. Conclusion

Our systematic studies of the 6,6'-substituted bridged, binaphthyl chiral dopants suggested that the |HTP| and $HTP_{t.d.}$ values were significantly affected by 6,6'-substituents of binaphthyl chiral dopant.

Acknowledgment

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Reference

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