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Wide blue phase range of chiral nematic liquid crystal doped with bent-shaped molecules

Zhigang Zheng, Dong Shen\textsuperscript{1} and Pei Huang

Department of Physics, East China University of Science and Technology, Shanghai 200237, People’s Republic of China
E-mail: shen@ecust.edu.cn

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Abstract. A wide blue phase range of 29°C is induced by a bent-shaped molecule that is doped in chiral nematic liquid crystals. The physical mechanisms of this effect are investigated through experimental comparisons and molecular simulations. The results obtained indicate that the wide temperature range is closely related to the lower interfacial tension between liquid crystals and defects, and the shrinkage of the radius of the defect core after the bent-shaped molecules are doped in the systems. Apart from this, extending the rigid body of the bent-shaped molecules leads to an increase in the biaxiality and dipole moment, which are the two additional important factors for obtaining a stable blue phase. This study provides new insights into broadening the liquid crystal blue phase.

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\textsuperscript{1} Author to whom any correspondence should be addressed.
1. Introduction

In recent years, the liquid crystal blue phase that normally exists in highly chiral systems has attracted wide attention from many researchers because of its intriguing structure. The blue phase is usually observed on cooling from the isotropic to the chiral nematic phase, with a structure of self-assembled three-dimensional cubics formed by double-twisted arranged liquid crystal cylinders [1]. Such an arrangement possesses optical isotropy, selective reflection to circular polarized beams, a reflective band switched by external fields and microsecond response. These characteristics show the potential application of blue phase in large-screen flat panel displays and tuneable photonic band gap materials [2]–[5]. However, the main technical difficulty of the applications is the very narrow temperature range of the phase, typically a few kelvins [6]. A lot of effort has been put into resolving this problem, mainly divided into two kinds: one is the polymer-stabilized blue phase (PSBP), which was first proposed by Kikuchi et al., obtained in the temperature range of over 60°C [7]. The other is directly synthesizing blue phase liquid crystals; representative examples are (i) the dimer liquid crystal with large flexoelectricity that has 44°C blue phase, reported by Coles et al. [8], and (ii) the T-shaped molecules and the binaphthyl derivative with temperature ranges of 13 and 29°C, contributed by Yoshizawa et al [9, 10]. Although some other ways have also been used to broaden the blue phase range, such as hydrogen-bond LCs and nanoparticle stabilization [11, 12], their physical mechanisms are basically similar to the above two kinds.

In 2003, Nakata et al. [13] noticed an exotic phenomenon that the blue phase can be induced by doping some bent-shaped molecules into the chiral nematic liquid crystal (N*LC). This result is very exciting; however, the blue phase range is very narrow, not exceeding 5°C, and the study of this mechanism is only preliminary. Later on, there was no progress in related studies.

In this paper, we report a much wider blue phase range induced by doping a kind of bent-shaped molecule with a strong biaxiality. The effects of the molecular structure on the temperature range are investigated here with experimental comparisons and molecular simulations. The results indicate that the mechanisms of such a wide blue phase range are different from normal explanations. Hence, it is believed that doping bent-shaped molecules may be another convenient method for obtaining a wide blue phase range.

2. Experiments and results

In the experiments, four kinds of doped systems are prepared by mixing the N*LC host and bent-shaped molecules. The N*LC host contains 67.2 wt% eutectic nematic liquid crystals (SLC-9023, from Slichem Co. Ltd) and 32.8 wt% chiral dopant R811 (from Merck Co. Ltd). The texture and phase transition of the N*LC host are tested by using a polarized optical microscope. There is no blue phase existing on cooling, and the transition temperature from isotropic to nematic is 79.3°C. Four kinds of bent-shaped molecules are synthesized by our laboratory (the chemical structures are shown in figure 1) and doped into the host, all with the same concentration of 7 wt%. These syrups are injected into a 12 µm thick cell and observed by using a polarized optical microscope with a crossed polarizer. The temperature of the sample is precisely controlled by the hot stage with a cooling rate of 0.5°C min⁻¹.

It is surprising that the blue phase is found in all of the samples. The phase transitions and temperature ranges of the samples are tested and compared with each other. As shown in
Table 1. Chemical composition of the samples, their phase transition and the blue phase range.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N°LC (93 wt%)</th>
<th>Dopant (7 wt%)</th>
<th>T_{iso–BP} (°C)</th>
<th>T_{BP–N°} (°C)</th>
<th>Range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>67.2 wt%</td>
<td>B1</td>
<td>80.9</td>
<td>70.3</td>
<td>11</td>
</tr>
<tr>
<td>D2</td>
<td>NLC+</td>
<td>B2</td>
<td>80.4</td>
<td>72.2</td>
<td>8</td>
</tr>
<tr>
<td>D3</td>
<td>32.8 wt%</td>
<td>B3</td>
<td>82.5</td>
<td>53.4</td>
<td>29</td>
</tr>
<tr>
<td>D4</td>
<td>R811</td>
<td>B4</td>
<td>82.3</td>
<td>59.5</td>
<td>23</td>
</tr>
</tbody>
</table>

*All of the phase transition temperatures were tested on cooling.

Figure 1. The chemical structure and the atomistic models of the bent-shaped molecules. The dipole moments (\(\mu\)) and the bent angles (\(\theta\)) are labeled.

Figure 2 gives polarized optical micrographs of D3 at isotropic, blue and chiral nematic phases. As shown, when D3 is cooled from the isotropic state gradually, a blue fog state appears first, which is
one of the thermodynamic stable blue phases, BP III (figure 2(b)); if we continue to decrease the temperature, a colored platelet is observed that is the typical optical texture of BP I, the other stable phase with a body-centered cubic lattice (figures 2(c)–(e)), and the color is reflected by the lattice; further cooling to a temperature near chiral nematic, the blue phase transitions to a brightly flowing texture (figure 2(f)), which is the chiral nematic. It should be mentioned that the melting point of the four bent-shaped dopants is over 140°C, which is much higher than the $T_{\text{Iso-BP}}$ given in table 1, because there is only a very small amount of such materials contained in the mixed systems. In addition, the isotropic state of these mixtures observed by a polarized optical microscope is uniformly dark (as shown in figure 2(a)). These results indicate better miscibility among LCs, R811 and the dopant. The arrangement of LCs and the dopant should be noted. As observed in experiments, LC molecules are twisted-arranged under the role of chiral R811 and exhibit chiral nematic phase with only one helical axis, in the absence of bent-shaped molecules in the mixture. On the addition of bent-shaped materials, the blue phase, with double-twisted arrangement of LCs, is induced. We consider that the emergence of the blue phase is closely related to the strong interactions between this kind of material and LCs, and the double-twisted arrangement of LCs is induced only if the bent-shaped molecules are twisted-arranged. Such an arrangement is possible in the mixed system, because of the good miscibility of chiral R811 and bent-shaped molecules; in addition, their molecular interaction is also very strong; however, if the bent-shaped molecules are arranged as nematic, such a double twisted arrangement is impossible. Hence, the arrangement of bent-shaped molecules is supposed to be twisted, although which phase of them is exhibited in the mixture has not been confirmed exactly. But how do bent-shaped molecules induce the blue phase, or in other words, what are the mechanisms underlying such experimental results? We investigate all these, combining experiments with molecular dynamics, as follows.

It is well known that the blue phase is a coexisting state of cubic lattices and defects. Since the generation of defects is associated with the energy consumption of the system, the entire system becomes unstable. Normally, the gain from a strong twist will reduce this consumption and make the whole system stable, so the blue phase is often found in high-chirality materials [1]. Do the bent-shaped dopants increase the twist energy of system? We compare the reflective band of the host system with all the other samples at the same temperature.
of 45 °C (the systems are chiral nematic), but only a small red shift (about 2–3 nm, tested by using a spectrometer) is found after bent-shaped molecules are added. The result indicates that the twist energy is almost invariant after doping.

In addition, it is also shown that there is a great difference in the blue phase range among the above samples, which may be found by the chemical structure of bent-shaped molecules; hence molecular simulations are carried out to better understand this phenomenon.

3. Molecular simulations and an analysis of the results

The stability of the blue phase depends on a well-arranged double-twisted LC and a stable defect, all of which are related to the interfacial energy between LCs and defects [7, 19]. Hence, we first study the interfacial energy and its effect on the blue phase. The doping effect on interfacial energy is calculated and analyzed by using molecular dynamics. An LCs/defect double-layer model is constructed at first for this calculation. The defect layer is easily simulated by an amorphous mixture of isotropic LCs and bent-shaped molecules, whereas the double-twisted LC layer is very complicated and difficult to construct, so some approximations should be used here. At the interface of the double-twisted cylinder, the director field locally approaches the single twist [14]; thus, the arrangement is simply in accordance with the law,

\[ \mathbf{n}(r) = x \cos(q \times \Delta \rho) + y \sin(q \times \Delta \rho), \]  

where \( q \) is the wavevector and equals \( 2\pi / P \), \( P \) is the period of the twist and \( \Delta \rho \) is a very small value along the radius of the cylinder. Consider that the interfacial energy is only related to the molecules on the surface that is normally several nanometers thick, but the period of the twisted structure is always hundreds of nanometers; that is, \( \Delta \rho \ll P \), \( q \times \Delta \rho \approx 0 \). Thus, the modulus of \( \mathbf{n}(r) \) is approximately equal to 1. Hence, the surface alignment of LCs can be replaced by the well-aligned nematic layer.

Using this approximate model, fully atomistic simulations of double layers are carried out under a polymer consistent force field (PCFF) [15], and thermo-relaxed in the NVT canonical ensemble using the Anderson thermostat with a time step of 1 fs [16]. Let the interfacial energy be represented as \( E_{\text{int}} \); the total energy of the double layer is \( E_0 \); the energies of the LC layer and the defect layer are \( E_{\text{LC}} \) and \( E_{\text{def}} \), respectively, and satisfy the following expression [17]:

\[ E_{\text{int}} = E_0 - (E_{\text{LC}} + E_{\text{def}}), \]  

from which \( E_0 \), \( E_{\text{LC}} \) and \( E_{\text{def}} \) can be calculated according to PCFF equations [16]. The calculated interfacial energies of the doping systems are given in table 2; minus in the table means energy consumption to form the layer structure. It is evident that the interfacial energy decreases after the bent-shaped molecule is doped. This is because of the large molecular volume of the dopant, which extends the distance between molecules and decreases the van der Waals energy of the system. A similar effect was also noted in the experiments of Klosterman et al [18] when they studied LC alignment on the octanoic acid-doped surface.

Combining molecular dynamics with elastic theory, two important points can be illustrated: firstly, the bent-shaped dopant induces the blue phase; secondly, the B3 molecule widens the blue phase range. As expressed by the elastic theory of the double-twisted LC, the total energy is [19]

\[ W = -1.4 \pi K + \pi R \sigma, \]
Table 2. Interfacial energies of the simulated layers.

<table>
<thead>
<tr>
<th>Layer model</th>
<th>$E_{\text{int}}$ (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LC[Iso]/LC[N]</td>
<td>$-405.4^b$</td>
</tr>
<tr>
<td>LC + B1/LC[N]$^a$</td>
<td>$-255.4$</td>
</tr>
<tr>
<td>LC + B2/LC[N]</td>
<td>$-238.4$</td>
</tr>
<tr>
<td>LC + B3/LC[N]</td>
<td>$-64.4$</td>
</tr>
<tr>
<td>LC + B4/LC[N]</td>
<td>$-68.4$</td>
</tr>
</tbody>
</table>

$^a$ LC + Bi/LC[N] ($i = 1, \ldots, 4$) represents the layer doped with Bi. LC + Bi is an amorphous mixture of LCs and the dopant Bi, simulated as a defect layer; and LC[N] is a well-aligned liquid crystal, simulated as a double-twisted layer.

$^b$ Minus means energy consumption to form the layer.

where $K$ is the elastic constant under one-constant approximation, $R$ is the radius of double-twisted cylinders and $\sigma$ is the interfacial tension, which is proportional to the interfacial energy. Provided that the double-twisted structure is more stable than the cholesteric one, $W < 0$ should be satisfied. Thus,

$$R = \frac{\pi}{q} = \frac{P}{2} < 1.4 \frac{K}{\sigma}. \tag{4}$$

In the N*LC host, no blue phase is found, so $R_0 > 1.4(K/\sigma)$. After doping bent-shaped molecules, the interfacial energy decreases, which leads to a decrease in the interfacial tension $\sigma$. In addition, the rigidity of the system is enhanced after doping because of the inflexibility of bent-shaped molecules, so that the elastic constant is increased. In the light of the above analyses, the ratio $K/\sigma$ is enlarged; thus $R_0 < 1.4(K/\sigma)$ can be achieved, and the blue phase is induced.

The interfacial energies of the layer models are given in table 2. Those of LC + B3/LC[N] and LC + B4/LC[N] are much lower than those of the other two (LC + B1/LC[N] and LC + B2/LC[N]), whereas from a comparison of their chemical structures, the elastic constants of the former two are larger than those of the latter two. According to equation (3), the first term is decreased and the total energies of the former two systems are smaller, so the double-twisted arrangements in the former two are more stable. This analysis agrees well with our experimental results, which indicate that the blue phase ranges of samples D3 and D4 are twice as wide as D1 and D2 (shown in table 1). The interfacial energy of LC + B3/LC[N] is the lowest; thus, it is reasonable that its blue phase range is the widest among all of the samples. This is also consistent with the experimental result, which shows the largest blue phase range of 29°C for sample D3.

However, the interfacial effect caused by the bent-shaped dopant is only one aspect of the blue phase. In addition to that, there are some other potential factors. Consider the elastic energy per unit defect. It can be expressed as the following equation [7]:

$$F = a(T_{\text{ISO-BP}} - T) \pi r^2 + 2\pi r \sigma + \frac{1}{4} \pi K \ln\left(\frac{r_{\text{max}}}{r}\right) - \pi (K_{22} + K_{24}), \tag{5}$$

in which $a$ is the constant associated with the Boltzmann constant, $T_{\text{ISO-BP}}$ is the phase transition temperature between isotropic and blue phases of the mixture and $T$ is an arbitrary temperature below the transition point. $r$ is the radius of the defect core, $r_{\text{max}}$ is the cut-off radius, the same as defined in [7]. $K$ is the elastic constant of the single-constant approximation, $K_{22}$ and $K_{24}$.
are the twist and saddle splay elastic constants. As defined above, \( \sigma \) is the interfacial tension between LCs and defects. The first term of equation (5) represents the increase in energy with decreasing temperature \( T \). The second term is the interfacial energy between LCs and defects. The third term gives the energy outside the defect, but inside the cut-off radius. The last term is a minus term, which decreases the total free energy below zero, and is only determined by \( K_{22} \) and \( K_{24} \).

It is found that the free energy is directly associated with the radius of the defect core, \( r \). Change in \( r \) affects the free energy of the defect and thus affects the stabilization of the blue phase. The first two terms in equation (5) are proportional to \( r \), and will decrease with it. The relationship between \( r \) and the third term is more complicated; however, for one thing, the cut-off radius, \( r_{\text{max}} \), decreases with \( r \) and thus the change in \( r_{\text{max}} / r \) is very small; for another, the trend of the logarithmic function with \( r \), \( \ln(r_{\text{max}} / r) \), is the slowest compared with the former two (square function \( r^2 \) of the first term and linear function \( r \) of the second); that is to say, the third term plays a secondary role in the total free energy. Hence, decreasing \( r \) leads to a reduction of free energy.

Many studies have indicated that the mesogenic part in molecules can control the alignment of LCs [9, 13, 19, 20]. Hence, we consider that with the doping of bent-shaped molecules, isotropic LCs near the interface between the defect core and the double-twisted cylinder will be realigned orderly by the rigid mesogenic body of bent-shaped molecules and the strong dipole moment interaction. Such realignment leads to shrinkage of the defect core; thus the free energy decreases according to equation (5). This is very difficult to investigate from the experiments, but is easy to investigate using molecular dynamics methods. The order parameters of LCs in the defect core with some bent-shaped molecules added are calculated and they are used to reflect the effect of doping on the shrinkage of radius. A high-order parameter means a strong effect brought about by bent-shaped molecules; thus the radius, \( r \), is smaller. The theoretical expression of the order parameter (\( S \)) used here is the same as the conventional second-order Legendre polynomials [16],

\[
S = 0.5[3(\cos^2 \theta_{ij}) - 1],
\]

where \( \theta_{ij} \) is the director angle between two arbitrary LC molecules, and \( \langle \rangle \) is the statistical average. Five defect models, without bent-shaped dopant and with B1, B2, B3 and B4 doped, are constructed as mentioned above and the LC order parameters in these cases are calculated with equation (6); the results are shown in figure 3. It is evident that the order parameter is

![Figure 3. The calculated order parameter of LCs in the defect core.](http://www.njp.org/)
increased in the doping systems, which predicts a decrease of the radius of the defect core on the addition of bent-shaped molecules. Thus, according to equation (5), the elastic energy of the defect decreases with the radius, $r$. Figure 3 also indicates that the order parameters of B3- and B4-doped systems are much higher than those of B1- and B2-doped systems. For the former two, the calculated results are $0.40 \pm 0.08$ and $0.42 \pm 0.08$, respectively, which are almost two and a half times as high as the latter two, $0.18 \pm 0.05$ and $0.15 \pm 0.05$. Hence it can be considered that the effects of B3 and B4 molecules on the shrinkage of radius are reasonably stronger than those of B1 and B2, and then the blue phases of B3- and B4-doped systems are more stable. However, there is no evident difference in blue phase ranges between the mixtures doped with B1 (B3) and B2 (B4), due to their similar chemical structure. Such theoretical analyses are in agreement with the experimental results given in table 1.

In addition, some experimental and theoretical works suggested that molecular biaxiality plays an important role in the blue phase [9, 10, 14]. Hence we investigate the chemical structure of bent-shaped molecules by the semi-empirical quantum chemistry algorithm, AM1 [21]. The optimized geometry and dipole moment of molecules are given in figure 1. As shown in the atomistic models, the geometries of the molecules are bent, which may generate the biaxiality. The axes of the bent-shaped molecules are represented in the model by dashed lines, and the bent angle ($\theta$) of the molecules has been labeled. Our calculated value is a little different from the estimated one, because of the tail group and the extension of the rigid body, but the relationship between the bent angle and the structure is the same as that mentioned by Takezoe and Takanishi [22]. Apparently, the biaxiality of molecules is proportional to their bent angle, and molecules with longer rigid body possess larger bent angle. Of the four molecules, the bent angles of B3 and B4 are 52° and 50°, respectively, which are about 10° larger than the bent angles of the other two, B1 and B2; thus the biaxiality of B3 and B4 is more evident and their capabilities to induce the blue phase are stronger, so the blue phase range of B3- and B4-doped systems, D3 and D4, is much wider than that of the other two systems, D1 and D2. That is to say, the longer the rigid body the larger the bent angle, thus leading to more stable blue phase. Therefore, from the molecular geometry point of view, the mechanism of the induced blue phase can be derived and depicted as in figure 4: due to the coupling between the chirality
of R811 and the biaxiality of bent-shaped molecules, the double-twisted arrangement of LCs is induced and the blue phase appears simultaneously. In addition, it is noteworthy that the dipole moment of bent-shaped molecules has a significant impact on the stabilization of the blue phase. A strong dipole moment of the molecules leads to greater interaction with LCs and strengthens the biaxiality [23], which is beneficial for the formation of a double-twisted structure; as a result, the stability of the blue phase is enhanced. The calculated dipole moment of B3 is 4.002 D, which is a little larger than that of B4, 3.857 D. Hence the blue phase range of the B3-doped sample D3 is 6 °C wider than that of D4, although their bent angles are almost the same.

4. Conclusions

The bent-shaped molecule-induced blue phase was studied, and a wide blue phase range of 29 °C was obtained. Some mechanisms of this effect were analyzed by using molecular simulations. The results indicate that doping bent-shaped molecules leads to a decrease in interfacial tension, an increase in the elastic constant and shrinkage of the defect core radius, which decreases the elastic energies of double-twisted LCs and the defect. A lower elastic energy is important for inducing a stable double-twisted arrangement. Moreover, extending the rigid body of bent-shaped molecules increases their biaxiality and dipole moment, which are the other aspects for inducing the blue phase, and helpful in enhancing its stability. Although some of these studies were theoretical, they provide new insights for understanding the mechanism of the induced blue phase from the molecular point of view. The study indicates that doping bent-shaped molecules may be another convenient method for obtaining a stable liquid crystal blue phase.

Acknowledgments

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