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Effect of Bent-Shaped Dopant on a Chiral Structure – Microscopic Model

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The position of the bent-shaped molecule when it is found in a chiral structure is discussed. Although the bent-shaped molecule is achiral by itself, its position and orientation can be recognized as structurally chiral. It is shown that due to the special shape and structural chirality, chiral structures of initial system become more enhanced.

Keywords: bent shaped molecules; cholesteric liquid crystal; structural chirality

INTRODUCTION

It is well known that doping of achiral systems with chiral dopants induces chiral properties and/or chiral structures in host systems. Naturally, doping of chiral systems with achiral dopants results in less emphasized chiral properties like longer periods of helicoidal modulations, smaller chiral polarization and similar. But recently, a surprising effect was found. When achiral bent-shaped molecules popularly called "bananas" are doped in a chiral system like chiral nematic or tilted chiral smectic, an enhancement of typical chiral macroscopic properties as shortening of the period of helicoidal modulation and/or appearance of blue phases was observed [1–3].

In this report we present a microscopic model that shows the mechanism by which a bent-shaped dopant additionally stimulates the nonhomogeneity of the initially already nonhomogeneous host system. We show that bent-shaped molecules adopt the position and orientation that is recognized as a structural chirality. We also introduce a chiral parameter that might be used as a measure of average chirality of a dopant.

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THEORY

Bent-shaped molecules consist of two branches structured similarly as typical elongated molecules forming chiral nematic and chiral tilted smectics. For most common molecules, the two branches form an angle of approximately 120°. When bent-shaped molecules are doped into the system of ordered elongated molecules, they favour position and orientation where branches are as parallel as possible with elongated molecules in the vicinity. This interaction between the dopant molecule and the host system can be phenomenologically expressed as

$$F_b \approx -(\vec{n}\cdot\vec{n}_1)^2-(\vec{n}\cdot\vec{n}_2)^2. \tag{1}$$

Here $\vec{n}$ is a local director of the host at the position ob molecular branches. Instead of describing bent-shaped molecule with the two "branch directors" $\vec{n}_1$ and $\vec{n}_2$ as shown on Figure 1, we express the orientation of the bent-shaped molecule with two vectors given as a sum and a difference of two "branch directors"

$$\begin{aligned}\vec{n}_b &= \vec{n}_1+\vec{n}_2\\ \vec{p}_b &= \vec{n}_2-\vec{n}_1\end{aligned} \tag{2}$$

hence

$$\begin{aligned}\vec{n}_1 &= \vec{n}_b+\vec{p}_b\\ \vec{n}_2 &= \vec{n}_b-\vec{p}_b.\end{aligned} \tag{3}$$

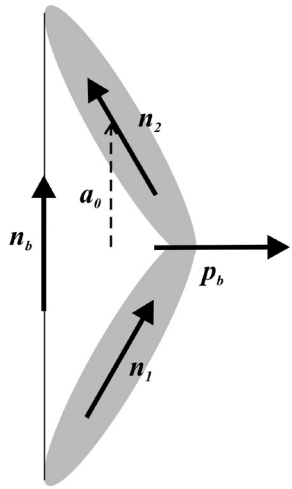

FIGURE 1 Branch directors, tilt and polarization of the bent-shaped molecule.

Here the director of the bent-shaped molecule $\vec{n}_b$ has a similar meaning as a nematic director and it is used for a single studied bent shaped molecule. It can be normalized to the unit length without any losses of generality. However, $\vec{p}_b$ is a proper vector. The description of the molecular shape i.e., the angle between the branches, can be obtained by the non-unit length of the $\vec{p}_b$. The vector $\vec{p}_b$ is usually called *polarization* since bent shaped molecules posses a dipolar moment parallel or antiparallel to the direction of $\vec{p}_b$. An analysis of the interaction given by Eq. (1) shows that in the achiral nematic or homogeneously tilted smectics bent shaped molecule orient with the polarization $\vec{p}_b$ parallel to the host director, if the angle between branches is smaller than 90°. More elongated bent shaped molecules orient the director $\vec{n}_b$ parallel to the host director. The orientation of the second vector needed for the description of the bent-shaped molecular orientation is undefined in both cases. In this report we consider only more elongated bent-shaped molecules that are consistent with the shape of dopant molecules used in reported experiments [1–3].

To account for the structural chirality of the host, the spatial variation of the host director is considered. Since a typical branch of the bent-shaped molecules is of the same length as typical elongated molecules of the host, we could expect that the bent-shaped molecule will adopt the orientation which could also benefit from the nonhomogeneity of the host. We consider only systems where changes of local director are continuous. The small changes of the local director of the host can be expressed as

$$\vec{n}(\vec{r}+d\vec{r}) = \vec{n}(\vec{r}) + d\vec{r}\cdot\nabla\vec{n} + \frac{1}{2}d\vec{r}\cdot(d\vec{r}\cdot\nabla(\nabla\vec{n})). \tag{4}$$

The phenomenological description of the bent-shaped molecular interaction from Eq.(1) using Eq. (3) with a nonhomogeneous host is

$$\begin{aligned} F \approx & -2(\vec{n}\cdot\vec{n}_b)^2 - 2(\vec{n}\cdot\vec{p}_b)^2 + 4((\vec{a}\cdot\nabla\vec{n})\cdot\vec{n}_b)(\vec{n}\cdot\vec{p}_b) \\ & + 4((\vec{a}\cdot\nabla\vec{n})\cdot\vec{p}_b)(\vec{n}\cdot\vec{n}_b) - 2((\vec{a}\cdot\nabla\vec{n})\cdot\vec{n}_b)^2 - 2((\vec{a}\cdot\nabla\vec{n})\cdot\vec{p}_b)^2 \\ & - 4(\vec{a}(\vec{a}\cdot\nabla(\nabla\vec{n}))\cdot\vec{n}_b)(\vec{n}\cdot\vec{n}_b) - 4(\vec{a}(\vec{a}\cdot\nabla(\nabla\vec{n}))\cdot\vec{p}_b)(\vec{n}\cdot\vec{p}_b). \end{aligned} \tag{5}$$

In order to analyse effects of the dopant on the structure we consider a typical chiral system – the helicoidally modulated chiral nematic with a pitch extending over a few 1000 molecular thicknesses. For chiral nematics continuous changes of the host director are more than appropriate. The spatial dependence of a director can be written as

$$\vec{n} = \{\cos qz, \sin qz, 0\} \tag{6}$$

Without a loss of generality, we can analyze the interaction at $z = 0$. We assume also that the angle between branches is close to the typical value 120°. Therefore the director $\vec{n}_b$ is parallel to the local director $\vec{n}$ and $\vec{p}_b$ is perpendicular to it. The interaction energy that appears due to the nonhomogeneity of the surrounding is

$$a\, n_{b,x}^2 + f_b q\, n_{b,x}\, n_{b,z}\, p_{b,y} + k_d q^2\, n_{b,z}\left(n_{b,x}^2 - p_{b,y}^2\right). \tag{7}$$

Here $a\, n_{b,x}^2$ gives the interaction with the nonmodulated nematic surrounding, the parameter f_b gives the induced chiral interaction and the parameter k_d describes the "elastic" properties of the dopant molecule. The last term is for the considered geometry always positive and discourages deviations of the director $\vec{n}_b$ from the parallelism with the local director.

However, the wave vector of the modulation can be positive or negative depending on the chirality of the host. The second term therefore favours orientations where components $n_{b,x}$ and $p_{b,z}$ will have opposite signs for positive q and equal signs for negative q. Bent shaped molecule will therefore adopt the position where director would tilt perpendicularly to the both – the local cholesteric director and to the polarization p_b and the favourable tilt direction will be defined by the direction of the polarization $p_{b,z}$, Figure 2.

Additional effect becomes also evident. While in a nonmodulated nematic surrounding all perpendicular directions of $\vec{p}_b$ are equivalent, here the decrease of the $p_{b,y}$ value that appears due to the rotation of the polarization around the director direction increases the energy. Therefore the preferable orientation of polarization $\vec{p}_b$ is perpendicular to the axis of the helicoidal modulation.

RESULTS AND DISCUSSION

If a number of molecules are doped into the initially already modulated system, the dopant will affect the host in several ways. The dopant will adopt the position and orientation that depends on the magnitude of the wave vector of helicoidal modulation as well as its sign (handedness).

Due to the dopant bent shape for which nonhomogeneous surroundings is more favourable, doping will promote shorter helicoidal periods of the host and will therefore change the effective phenomenological chiral properties. In systems where all dopant molecules will adopt one of the favourable positions and orientations, we expect that shorter pitches will be promoted. However, if the period of the helicoidal modulation of the host is very long, bent-shaped molecules

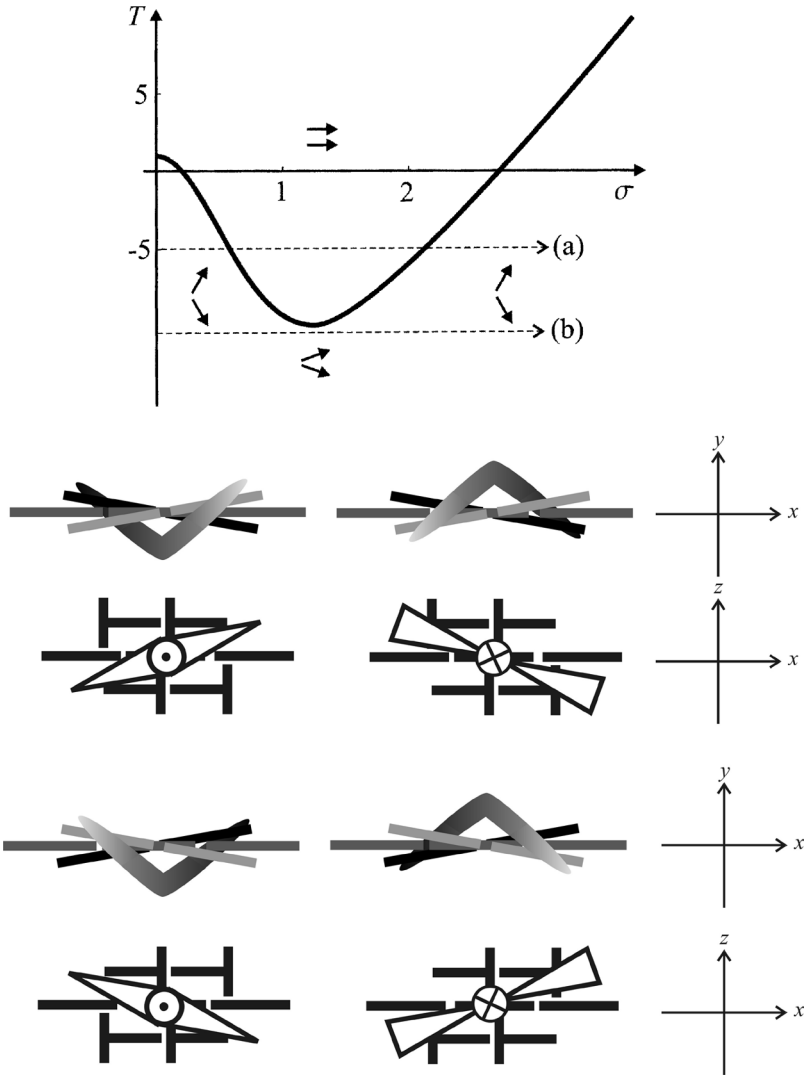

FIGURE 2 Position of the doped bent-shaped molecule in the helicoidally modulated chiral nematic. For the side view the nail notation is used. The two pictures above and the two pictures below represent oppositely chiral hosts, respectively. From upside view (the first and the third row) is clearly seen that the best parallelism of branches is obtained only for the drawn orientations of bent-shaped molecules.

would be only weekly affected by the nonhomogeneity and the rotation about the long axes will be still present. In this case, the effect of "dilution" of the chirality with the achiral dopant, would be observed [1]. However, if the temperature variation changes chiral or elastic properties drastically, the enhancement of chiral properties may also enter in such systems [3].

The orientation of the bent-shaped molecule has all the properties of the structural chirality. As an example, let us consider the chiral tilted smectics where layers are polar. In these systems chiral parameter as a pseudoscalar can be defined by three vectors – smectic layer normal, tilt order parameter and polarization as

$$\sigma = \left(\vec{\xi} \times \vec{p}\right)_z \tag{8}$$

where $\vec{\xi} = \{n_z n_x, -n_z n_y\}$ and $\vec{p}$ is the polarization. If the smectically ordered system is chiral, tilt induces polarity. The phenomenon is called "piezoelectric effect". On the other hand, polarization induced by external electric field induces tilt, and the phenomenon is called the "electroclinic effect". We expect that if the system possesses independent parameters of tilt and polarization, the structure that possesses both is chiral. The phenomenon was also observed in systems formed only of bent shaped molecules [4].

When achiral systems are doped with chiral dopants, chiral conformations of, in average achiral molecules, become more favoured and in the initially achiral system chiral properties are induced. When achiral molecules are doped in a chiral system, the interactions with chiral surrounding favour chiral molecular conformations and/or, as in the considered case, orientations with properties of chiral structure. In the second term in Eq. (7) we can recognize the same combination of average bent-shaped molecular "tilt" $n_{b,x}\, n_{b,z}$ and polarization $p_{b,y}$ as in the chiral parameter σ in chiral smectics. This chiral parameter has the same sign for two different combinations of tilt and polarization, Figure 2. It is positive if both have the same sign and it is negative if they have different signs. In a cholesteric liquid crystal where wave vector is positive, bent-shaped molecules orient with the negative chiral parameter and in systems from the opposite enantiomers they have the positive sign (Fig. 2). The magnitude of the chiral parameter σ depends on the order of the surrounding and its wave vector but reversely also influences wave vector since shorter pitches become more favourable. Thus, the chiral part of the interaction between the dopant and the host can be written in a simple form

$$f_b \sigma q. \tag{9}$$

The parameter f_b replaces (proportionally to the dopant volume fraction) chiral interaction between the host molecules. If the parameter is due to the structural chirality of the bent dopant larger than the chiral parameter of the host, it enhances the chirality of the whole sample.

CONCLUSIONS

To conclude, in the contribution the analysis of the interactions between bent-shaped dopants and chiral host with nonhomogeneous order is presented. A more thorough study of the chiral nematic systems shows that achiral bent-shaped molecules adopt the position and orientation which has all characteristics of structural chirality. The chiral parameter for the dopant is introduced and the phenomenological term, that gives the effect of the dopant structural chirality on the host is proposed. The results of the analysis are compared with known experimental observations.

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