PHYSICAL REVIEW E **67**, 061704 (2003)

Enhanced chirality by adding achiral molecules into the chiral system

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(Received 3 January 2003; published 17 June 2003)

It is generally accepted that the doping of chiral materials with achiral molecules diminishes the chirality of the system. Here we report the opposite phenomenon. It was found that the structural chirality of smectic phases made of rodlike molecules, Sm-C^* or Sm-C_A^* phases, measured as the reverse length of the helical pitch, is enhanced by adding small amount of achiral bent-shaped molecules. The effect is due to the chirality transfer between host and guest systems. Achiral bent-shaped molecules become structurally chiral due to the interactions with the chiral host that induces tilt and polar order of bent-shaped molecules. This induced chirality is then transferred back to the host.

DOI: 10.1103/PhysRevE.67.061704 PACS number(s): 61.30.Cz, 61.30.Eb, 61.30.Gd

The chirality was defined by Lord Kelvin in his Baltimore lectures in 1884: ‘‘I call any geometrical object or group of points chiral, and say it has chirality, if its mirror image cannot be brought into coincidence with itself.’’ [1]. This definition is valid for the macroscopic objects as well as for molecules. The molecular chirality was discovered several years later by Louis Pasteur [2], who proved that chiral molecules appear in two forms of opposite handedness, called enantiomers. In 1894, Pierre Curie showed a link between the molecular chirality and the chirality of the macroscopic structure: ‘‘When certain effects reveal a certain asymmetry, this asymmetry must be found in the causes that originated them. The opposite is not necessarily true . . . .’’ In other words, chiral properties of molecules can be transferred into the structures formed by groups of molecules. Some of the well known examples are crystals with chiral structures formed by chiral molecules and a double helix of DNA that is determined by the chirality of constituent amino acids. Nevertheless, the exact mechanism of the chirality transfer between the molecular and structural levels is still not well understood.

It is generally observed that when chiral system is doped by achiral molecules, the chirality of the initial system is diluted [3]. In this paper, we report the opposite effect. For studied systems, in contrast to general expectations, upon doping with achiral material the chiral host, structural chirality of the host is enhanced. The possible mechanism which extremely enhances the chirality of the initial system even for very low concentrations of dopants is presented.

For our studies we have chosen chiral polar smectic materials, which exhibit liquid crystalline phases with chiral structures. In these systems, a slight variation of either temperature or the enantiomeric excess influences a delicate balance between different interactions and results in the stability of numerous phases [4]. Doping such systems with other material might also influence the interactions significantly and might result in pronounced and easily observable changes of phase structures.

Some chiral liquid crystals have evident chiral structures. In chiral nematics the average direction of long molecular axis rotates in space, along the direction perpendicular to it, forming helicoidally modulated structure. In tilted smectics, where elongated, rodlike molecules are organized in layers but tilted away with long molecular axes from the layer normal, polar ferroelectric and antiferroelectric phases exist only when at least a fraction of constituent molecules is chiral. Moreover, similarly as in chiral nematics, chiral tilted smectics have the helicoidally modulated structure, e.g., the molecular tilt precesses around the cone when going from the layer to layer [5]. The period of the helicoidal modulation is called pitch. The larger the enantiomeric excess, the shorter is the pitch in the system; therefore, the pitch length can be used for the semiquantitative comparison of the chirality of systems. The pitch can be measured by selective reflection (SR) method. The light which incidents normally to the smectic layers, is reflected if its wavelength $\lambda = np$, where n is the average refractive index and p is the length of the pitch [6].

Several compounds, exhibiting chiral helicoidally modulated tilted smectic phases (Table I) which form ferroelectric (Sm-C^*) or/and antiferroelectric (Sm-C_A^*) phases, have been doped with a small amount (up to a few percent) of various achiral but bent-shaped molecules (Table II). The wavelengths of the SR light for undoped and doped systems were measured for free suspended film samples. In doped systems, the wavelength of SR was always shorter than that in undoped systems, indicating the shortening of the pitch, thus increased chirality of the doped system. The shortening of the pitch was observed in both the Sm-C^* and in Sm-C_A^* phases and became conspicuous with the concentration of the dopant (Fig. 1). The result is surprising since doping of the chiral system with achiral molecules has otherwise always resulted in a ‘‘diluted’’ chirality and consequently in an increase of the pitch length.

What is the possible mechanism responsible for this phenomenon?

This effect might arise from the intermolecular chirality transfer [7]. If the bent-shaped molecule is not flat but its branches are twisted, the two basic conformations with op-

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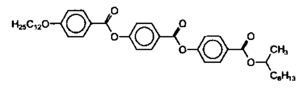
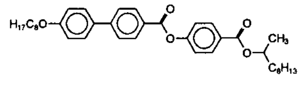
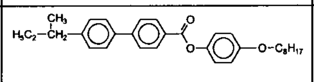
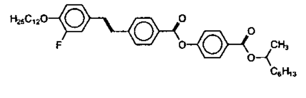
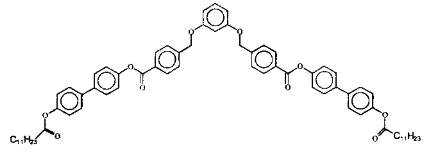
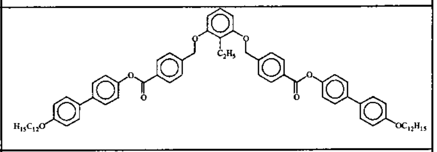
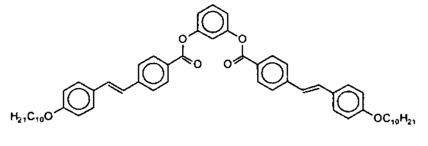
TABLE I. Molecular structures of host materials and phases, where the effects of doping were studied.

Host A		Sm C* and Sm C_A^*
Host B		Sm C_A^*
Host C		Sm C*
Host D		Sm C* and Sm C_A^*

posite chirality exist. The interactions with chiral host might favor one of the twisted, chiral conformations of the dopant. Induced enantiomeric excess of the bent-shaped material might enhance the chirality of the phase structure, i.e., shorten the helical pitch. However, it should be stressed that the helix shortening upon doping with achiral material is observed exclusively for the bent-shaped molecules. If the intermolecular chirality transfer is important, the effect should be observed for the broad class of materials, since every complex molecule forms a number of chiral conformations that could be stabilized in a chiral surrounding. Thus we have to consider also other mechanism that takes into account the unique shape of dopant molecules.

TABLE II. Molecular structures of dopants.

Dopant A	
Dopant B	
Dopant C	

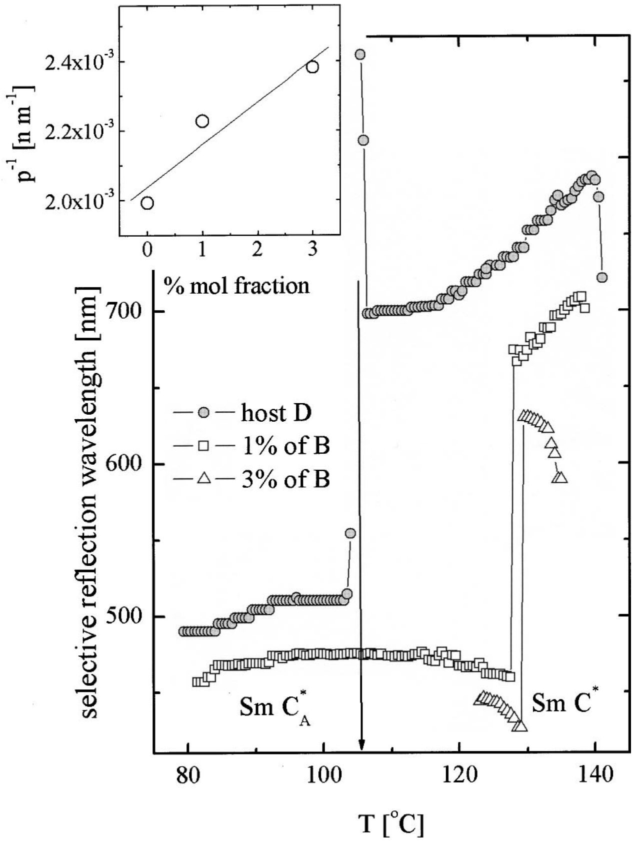


FIG. 1. Selective reflection of the undoped and doped systems where the Sm-C^* phase is stable at higher temperatures and the Sm-C_A^* phase is stable at lower temperatures. In both phases, upon doping the wavelength of the reflected light becomes shorter, indicating the shortening of the pitch, thus increase of structural chirality. As already pointed out in Ref. [10], the Sm-C_A^* is stabilized by doping. In the inset we give inverse pitch length vs concentration of the dopant for the Sm-C^* phase at 130C'.

In the achiral Sm-C phase, the tilt in neighboring layers is parallel [Fig. 2(a)] while in the achiral Sm-C_A phase the tilt in neighboring layers is antiparallel [Fig. 2(b)]. In chiral systems, chiral interlayer interactions between neighboring layers induce a slight deviation δ_0 from the (anti)parallelism, which results in the helicoidal modulations mentioned before. In this paper, we consider only changes of the tilt orientation from layer to layer in the Sm-C^* and Sm-C_A^* systems, therefore only interactions between nearest neighboring layers. The part of the free energy that gives interlayer interactions in the chiral undoped system can be written in its simplest form [8] as

$$G_{\mathrm{int},R}=\tfrac{1}{2}a_1(\boldsymbol{\xi}_j\cdot\boldsymbol{\xi}_{j+1})-\tfrac{1}{2}f_1(\boldsymbol{\xi}_j\times\boldsymbol{\xi}_{j+1})_z. \qquad (1)$$

In Eq. (1), the *rod tilt vector* $\boldsymbol{\xi}_j$ gives the projection of the average direction of the long rodlike molecular axes in the jth layer on the smectic plane [Fig. 2(a) above]. The parameter a_1 is negative if the Sm-C^* phase is stable and it is positive in the Sm-C_A^* phase. The parameter f_1 gives chiral van der Waals interlayer interactions and favors twisted tilt structure in neighboring layers. It has opposite signs for opposite enantiomers, thus, handedness of the helicoidal modulation is opposite. It is proportional to the enantiomeric excess and as a result systems with larger enantiomeric excess have shorter pitches. In studied systems where pitches of helicoidal modulations are a few hundred nanometers long, the parameter $|a_1|\gg|f_1|$.

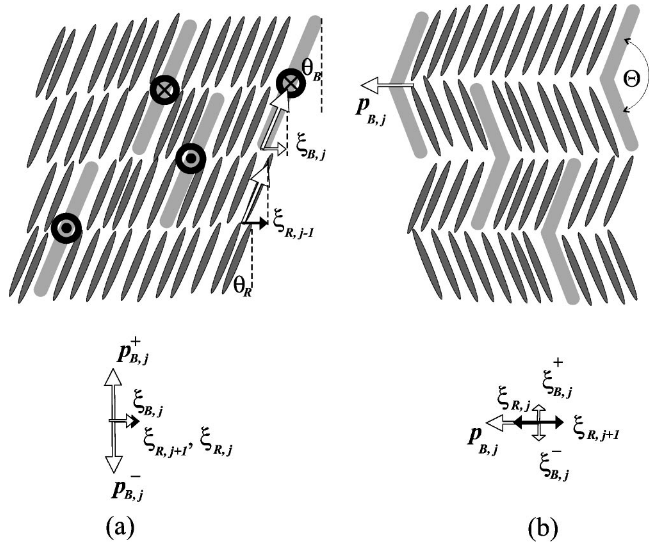


FIG. 2. (a) Above: schematic structure of doped achiral Sm-C phase. Below: Bananas adopt the tilted position in the two neighboring layers with equally probable directions $\boldsymbol{p}^+_{B,j}$ and $\boldsymbol{p}^-_{B,j}$. (b) Above: schematic structure of doped achiral Sm-C_A phase. Banana adopts the position in the two neighboring layers with the polarization oriented antiparallel to the difference of tilt vectors. Below: Bananas are locally tilted perpendicularly to $\boldsymbol{p}^+_{B,j}$ but both directions $\boldsymbol{\xi}^+_{B,j}$ and $\boldsymbol{\xi}^-_{B,j}$ are equally probable.

The bent-shaped molecule or as it is often called the banana molecule, consists of two connected, elongated branches, which form an angle $\Theta \approx 120°$ [Fig. 2(b) above]. Studied banana molecules are symmetric, with identical branches of comparable length with the length of host rodlike molecules.

When bananas are added to the achiral Sm-C or Sm-C_A phase, they adopt a position within two neighboring smectic layers [Figs. 2(a) and 2(b)] [9]. For the description of the banana position we use the subscript j for bananas which are placed in the jth and $(j+1)$st layers. For the description of the banana orientation we use the *banana tilt* vector $\boldsymbol{\xi}_{B,j}$, which is the projection of unit vector in the direction of the line joining the ends of the banana branches [Fig. 2(a) above], and the vector $\boldsymbol{p}_{B,j}$, which is given in Fig. 2(b) (above). It has the direction of the average electric dipole, which bananas posses, and therefore it is simply called the *banana polarization*.

In the achiral Sm-C phase bananas are tilted with the tilt vector $\boldsymbol{\xi}_{j,B}$ parallel to the tilt vector of rodlike molecules $\boldsymbol{\xi}_j$. Such orientation is favored due to the attractive van der Waals interactions, since it allows for the highest possible parallelism between banana branches and rodlike molecules. The banana polarization is perpendicular to the tilt plane and doubly degenerated, since the probability that the banana polarization forms an angle $\pm\pi/2$ with respect to the tilt plane is equal. Due to the van der Waals attraction, in the achiral Sm-C_A phase bananas are, on an average, nontilted while banana polarization $\boldsymbol{p}_{B,j}$ is in the tilt plane of host molecules and alternates its direction between layers. Since in achiral Sm-C_A bananas are not tilted and in achiral Sm-C not polarly ordered, in both phases they are structurally achiral [10].

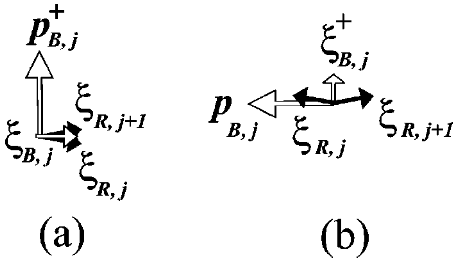


FIG. 3. In the chiral Sm-C^* phase (a) and in the chiral Sm-C^*_A phase (b), the banana tilt-polarization degeneracy is lifted and only one mutual orientation remains.

Also in the chiral Sm-C^* phase due to attractive van der Waals forces between banana branches and rodlike molecules, banana adopts orientation in which banana branches are as parallel as possible to the rodlike molecules [Fig. 3(a)]. This requires banana tilt vector $\boldsymbol{\xi}_{j,B}$ to be parallel to the average tilt vector of rods $\boldsymbol{\xi}_j$ in the two neighboring layers $(\boldsymbol{\xi}_j+\boldsymbol{\xi}_{j+1})/2$ and banana polarization $\boldsymbol{p}_{j,B}$ antiparallel to the difference of rod tilt vectors in neighboring layers $(\boldsymbol{\xi}_{j+1}-\boldsymbol{\xi}_j)/2$. Thus Sm-$C^*$ phase degeneration of the banana polarization direction is lifted. Since in the Sm-C^* phase banana molecules are tilted and polarly ordered, with the constant direction of axial vector given by $\boldsymbol{\xi}_{j,B}\times\boldsymbol{p}_{j,B}$, they become structurally chiral although the isolated banana molecule was achiral [10].

To account for the influence of the banana polarization on the interlayer interactions in the Sm-C^* phase, the free energy becomes

$$G_{\text{int}}=G_{\text{int},R}+\tfrac{1}{2}\Omega_p\boldsymbol{p}_{B,j}\cdot(\boldsymbol{\xi}_{R,j+1}-\boldsymbol{\xi}_{R,j}), \tag{2}$$

where G_{int} stands for the free energy of the doped system and $G_{\text{int},R}$ is given by Eq. (1). The term with the positive parameter Ω_p gives favorable antiparallel orientation of the banana polarization vector and the difference of the tilt vectors in neighboring layers of the rodlike system. Since the degeneracy of the banana polarization vector orientation is already lifted, we take its value p_B as a constant.

To find the structure of the doped chiral Sm-C^* phase, we assume that the helicoidally modulated tilt in the rodlike system is given by $\boldsymbol{\xi}_{R,j}=\theta_R(\cos j\delta,\sin j\delta)$, where δ gives the phase difference of the rodlike molecules in neighboring layers. The banana tilt is equal to the average tilt in neighboring layers of rodlike molecules, $\boldsymbol{\xi}_{B,j}=\theta_B[\cos(j+\tfrac{1}{2})\delta, \sin(j+\tfrac{1}{2})\delta]$, and the polarization $\boldsymbol{p}_{B,j}=p_B[-\sin(j+\tfrac{1}{2})\delta,\cos(j+\tfrac{1}{2})\delta]$ gives the orientation of the bananas placed with branches in the jth and $(j+1)$st layers. The free energy given in Eq. (2) is then

$$G_{\text{int}}=\frac{1}{2}a_1\theta_R^2\cos(\pm\delta)-\frac{1}{2}f_1\theta_R^2\sin\delta-\Omega_p p_B\theta_R\sin\left(\pm\frac{\delta}{2}\right), \tag{3}$$

where plus stands for the left handed helix in enantiomers with positive f_1. For small deviation δ we can use the harmonic approximation where $\cos\delta = 1-\delta^2/2$ and $\sin(\pm\delta) = \pm\delta$ and minimize the free energy with respect to δ. As a result we obtain

$$\delta = -\frac{f_1}{a_1} - \frac{\Omega_p p_B}{a_1 \theta_R} = \delta_0 + \frac{\Omega_p p_B}{|a_1|\theta_R}, \tag{4}$$

where δ_0 is the absolute value of the phase difference in the undoped system. In the doped system δ is enlarged, consequently the pitch is shorter and the structural chirality is enhanced. The effect, due to the change of the modulation handedness, is the same for both enantiomers.

In the Sm-C_A phase, banana molecules are oriented with their polarization in the direction of the difference between rod tilt vectors [Fig. 2(b)]. If the angle between banana branches is $\Theta > \pi - 2\theta_R$, the banana molecule could adopt the position where branches are parallel to the rodlike molecules only when rod tilts in neighboring layers are not in the same plane. Thus banana tends to tilt and locally induces nonantiparallelism of rod tilt vectors. In the achiral Sm-C_A banana tilt directions are equally probable, but in the chiral helicoidally modulated system, the tilt-polarization degeneration is lifted and, similarly as in the Sm-C^* phase, banana molecule becomes structurally chiral. In order to account for the preferable tilt in the direction of the average tilt in the neighboring layers, the free energy of the host system has to be modified as

$$G_{\mathrm{int}} = G_{\mathrm{int},R} + \tfrac{1}{2}\Omega_\xi \boldsymbol{\xi}_{B,j} \cdot (\boldsymbol{\xi}_{R,j+1} + \boldsymbol{\xi}_{R,j}). \tag{5}$$

In the expression, parameter a_1 in Eq. (1) is positive, since antiparallel ordering of the neighboring rodlike molecules is favored. The negative Ω_ξ gives the favored parallelism of the average rod and banana tilt. Following the same procedure as for the Sm-C^* phase, we get

$$\delta = \frac{f_1}{a_1} - \frac{\Omega_\xi \theta_B}{a_1 \theta_R} = \delta_0 + \frac{|\Omega_\xi|\theta_B}{a_1 \theta_R}. \tag{6}$$

Here δ_0 gives the absolute deviation from the antiparallel ordering of the neighboring rodlike molecules in the undoped system. Again, in the Sm-C_A^* phase of the doped system, δ is enlarged, the pitch is shorter, and the structural chirality is enhanced. The effect is equal for both enantiomers, since the sum of tilts in neighboring layers has opposite directions in opposite enantiomers.

Doped systems experienced shortening of the pitch for more than 100 nm even for very low concentrations of dopants. Why is the effect tremendous? The chiral parameter f_1 gives chiral interactions between parts of the molecules from different, i.e., neighboring interlayer interactions. We can assume that its magnitude is for small dopant concentrations given by $f_1 = f_{1,0}(1-c)$, where $f_{1,0}$ gives pure host and c gives the concentration of the dopant. On the other hand, parameters Ω_p and Ω_ξ give interactions between the banana branches and rodlike molecules and are comparable with intralayer intermolecular interactions. For low concentrations we can expect the proportionality to the dopant concentration as $\Omega_p = c\,\Omega_{p,0}$ or $\Omega_\xi = c\,\Omega_{\xi,0}$. The effective parameters a_1 and f_1 are changed for a comparable value. Since $|a_1| \gg |f_1|$, the elastic interlayer properties given by a_1 do not change significantly, but the relative change of the small chiral parameter f_1 is significant even upon slight doping already. The change of the absolute value of δ given in Eqs. (4) and (6) can be expressed in terms of concentration as

$$\Delta\delta = \delta - \delta_0 = c\left(\left|\frac{\Omega_p p_B}{a_1 \theta_R}\right| - \left|\frac{f_1}{a_1}\right| \right) \tag{7}$$

in the Sm-C^* phase and

$$\Delta\delta = \delta - \delta_0 = c\left(\left|\frac{\Omega_\xi \theta_B}{a_1 \theta_R}\right| - \left|\frac{f_1}{a_1}\right| \right) \tag{8}$$

in the Sm-C_A^* phase. In systems where host-dopant interactions are weaker than intermolecular interactions in pure host, we might expect lengthening of the pitch or ‘‘dilution of structural chirality.’’ When bananas are doped into the rodlike tilted smectic system, the opposite is true. Due to the special shape of the banana molecules, weak interlayer chiral interactions are partly replaced by strong essentially intralayer interactions and a drastic shortening of the pitch occurs even for very low concentrations of dopants.

In conclusion, we have studied the influence of the achiral bent-shaped dopant on the chiral polar smectic liquid crystalline system. In contrast to the general behavior, doping with achiral ‘‘banana’’ molecules results in the enhanced chiral properties of the doped system. As the chirality measure, the pitch length of the helicoidal modulation has been used. It has been shown that pitch decreases as the concentration of the achiral dopant increases, indicating the increase of the chiral properties of the initial system. Similar behavior was observed in the cholesteric phase [7] but was explained by the intermolecular chirality transfer; i.e., inherently achiral banana molecules take a twisted conformation by chirality transfer from the chiral host to the dopants. In tilted chiral smectics, we showed that another scenario is also possible. Achiral banana molecules become structurally chiral, e.g., the chiral host induces tilted and polarly ordered structure of bananas. As a result, the dopant with induced chirality transfers its chirality back to the host and the helical pitch becomes shorter.

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[1] H.G. Kuball, Liq. Cryst. Today **9**, 1 (1999).

[2] http://www.nature.com/nsu/000622/000622-10.html

[3] D. Demus, J. W. Goodby, G. W. Gray, H. W. Spiess, and V. Volkmar, *Handbook of Liquid Crystals* (Wiley-VCH, Weinheim, 1998).

[4] E. Gorecka, D. Pociecha, M. Čepič, B. Žekš, and R. Dabrowski, Phys. Rev. E **65**, 061703 (2002).

[5] R. Meyer, L. Liebert, and P. Keller, J. Phys. (France) Lett. **36**, L69 (1975).

[6] S. Chandrasekhar, *Liquid Crystals* (Cambridge University

Press, Cambridge, 1997).
[7] J. Thisayukta, H. Niwano, H. Takezoe, and J. Watanabe, J. Am. Chem. Soc. **124**, 3354 (2002).
[8] M. Čepič and B. Žekš, Phys. Rev. Lett. **87**, 085501 (2001).
[9] E. Gorecka, M. Nakata, J. Mieckowski, Y. Takanishi, K. Ishikawa, J. Watanabe, H. Takezoe, S.H. Eichhorn, and T. Swager, Phys. Rev. Lett. **85**, 2526 (2000).
[10] D.R. Link, G. Natale, R. Shao, J.E. Maclennan, N.A. Clark, E. Korblova, and D.M. Walba, Science **278**, 1924 (1997).