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Spontaneous helix formation in smectic liquid crystals comprising achiral molecules

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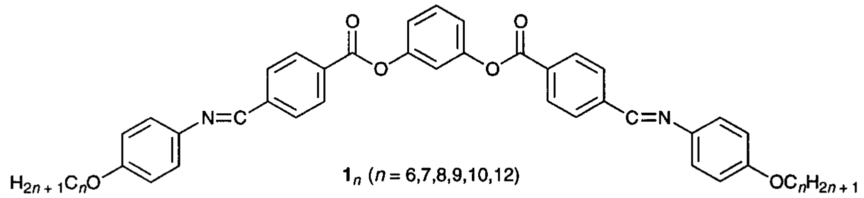
Spontaneous formation of two types of helical structure is observed in two smectic phases consisting of banana-shaped achiral molecules for the first time. Local optical resolution occurs to form spatially resolved helices of both handednesses.

Since the discovery of the first liquid crystalline material in 1888, helicity has proven to be the most fascinating topic of research in orientationally ordered mesophases.[1] The cholesteric mesophase was the first liquid crystal with helical structure to be found. Other phases, such as blue phases and the ferroelectric and antiferroelectric smectic phases, were shown to have helical arrangements of their constituent molecules. More recently, the helical smectic A phase, the so called twisted grain boundary (TGB) phase in which a discontinuous layer twist exists, has been found. In these helical phases, at least a fraction of the constituent molecules have an asymmetric carbon. This is the first report of spontaneous helix formation



1_n ($n = 6,7,8,9,10,12$)

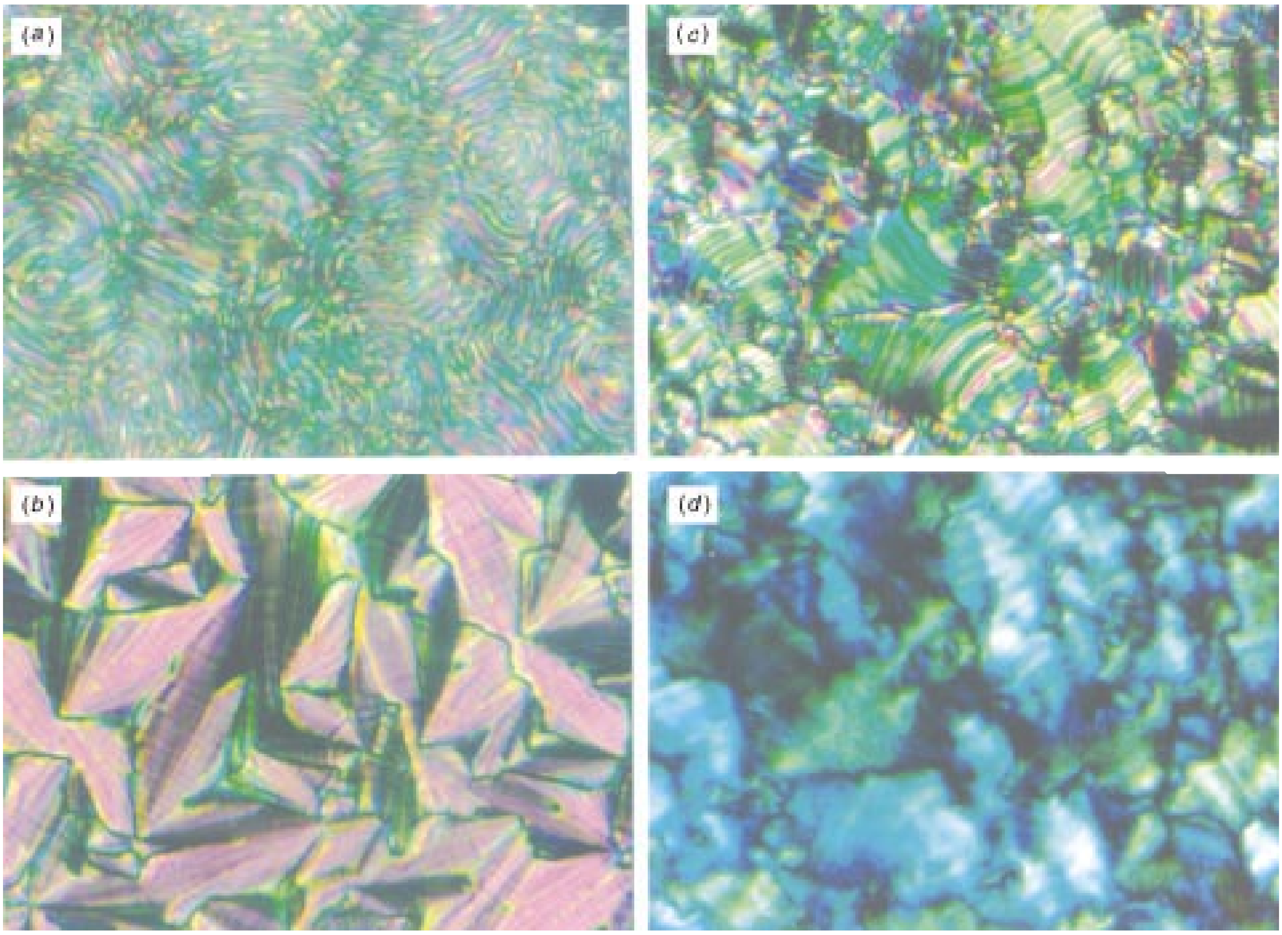


Fig. 1 Optical micrographs observed in a 5 μm thick homogeneously aligned cell of $\mathbf{1}_8$: (*a*) S_{X_1}, 0 V; (*b*) S_{X_1}, 50 V; (*c*) S_{X_2}, 0 V; (*d*) S_{X_3}, 0 V

Table 1 Transition temperatures of compounds $\mathbf{1}_n$

compound	transition temperature/°C						
	S_{X_3}		S_{X_2}		S_{X_1}		Iso
$\mathbf{1}_6$	●	144.9	●	158.5	●	173.1	●
$\mathbf{1}_7$	●	141.3	●	155.2	●	171.7	●
$\mathbf{1}_8$	●	139.7	●	151.9	●	173.9	●
$\mathbf{1}_9$	●	137.7	●	145.9	●	173.5	●
$\mathbf{1}_{10}$	●	138.4	●	144.4	●	172.7	●
$\mathbf{1}_{12}$	●		140.9		●	169.9	●

in fluid smectic systems comprised of achiral banana-shaped molecules.

The materials used were compounds $\mathbf{1}_n$ ($n = 6$, 7, 8, 9, 10, 12 and 16), which show three smectic phases, S_{X_1}, S_{X_2} and S_{X_3}, as shown in Table 1. According to X-ray diffraction, the smectic layer spacings are approximately the same as the lengths of the molecules in bent configurations.[2,3] X-Ray patterns also show the liquid-like association of molecules within a layer in the highest temperature S_{X_1}, whereas there is a two-dimensionally-ordered packing of molecules in S_{X_2} and S_{X_3}.

Figs. 1(*a*) and (*b*) show optical micrographs observed for the S_{X_1} phase of $\mathbf{1}_8$. Very strikingly, a fringe pattern characteristic to a helical structure is observed [Fig. 1(*a*)]. By applying an electric field of 50 V, the fringe pattern immediately disappears to give a fan-shaped texture [Fig. 1(*b*)]. As already reported, the S_{X_1} phase shows ferroelectricity with a spontaneous polarization of *ca.* 60 nC/cm^{-2}.[3] This ferroelectricity originates from the characteristic layer packing of banana-shaped molecules in which their bend direction is uniformly aligned within a layer, and the spontaneous polarization arises along the bend direction of molecule [see later, Fig. 3(*a*)]. Thus, the fringe pattern results from the helical structure with the in-layer polarization precessing along the layer normal, and its disappearance upon field application is due to the helix unwinding, as in the chiral S_C* phase.[4]

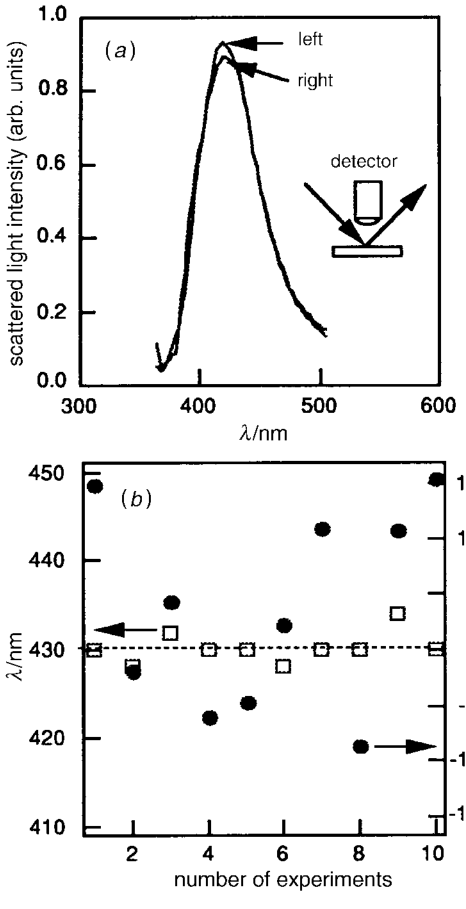


Fig. 2 (*a*) Spectra of scattered light measured for the blue S_{X_3} phase of $\mathbf{1}_8$ using right- and left-circularly polarized light. A detector was placed in front of the sample surface (see inset) so that the specular reflection of the obliquely incident light was avoided. (*b*) Peak wavelength and dichroic ratio, $(I_R - I_L)/(I_R + I_L)$, obtained for repeated measurements. Here I_R (I_L) stands for scattered light intensity of right- (left-)circularly polarized light.

There is no indication of helical structure in the S_{X_2} phase [see Fig. 1(*c*)], but the S_{X_3} phase looks like a blue phase,[5] as can be seen from the texture of Fig. 1(*d*), also suggesting a helical structure. In order to explore the origin of the blue colour in the S_{X_3} phase, the spectrum of the scattered light was measured. As shown in Fig. 2(*a*), a sharp reflection band was clearly observed. The peak wavelength around 430 nm corresponds to the blue reflection colour, which originates from a Bragg (selective) reflection due to a helical structure. To assess the handedness of the helix, the reflection measurements using right- and left-circularly polarized lights were made after heating the cell up to the isotropic phase and cooling it down to S_{X_3}. The results are shown in Fig. 2(*b*). While the wavelength of the selective reflection peak falls into a range of about 4 nm, the absolute value and the sign of the dichroic ratio are randomly distributed around zero. These facts indicate a delicate unbalance in the existence probability of two domains of right- and left-handed helices within the viewing spot; it is noteworthy that a significant unbalance can be produced by the addition of chiral dopants. Thus, we can safely conclude that a helical structure is spontaneously formed and its generation is determined by chance development, with nearly equal probability, of right- or left-handed helix.

It is interesting that the helical structure is formed along the different axes between the S_{X_1} and S_{X_3} phases. In S_{X_1}, the fringe patterns are superimposed on the fan-shaped texture. Hence, the molecules and the polarizations precess along the layer normal [see Fig. 3(*b*)]. On the other hand, S_{X_3} exhibits

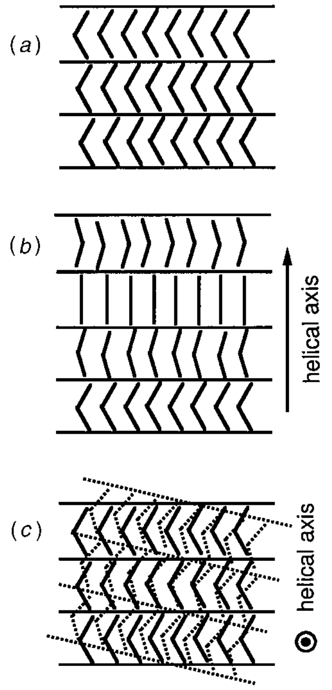


Fig. 3 Schematic illustrations of the molecular packing and the smectic layer structures. (*a*) Banana-shaped molecules stack with the same bend direction to form a layer. The spontaneous polarization appears along the bend direction parallel to the layer. (*b*) The helical structure in the S_{X_1} phase is formed along the layer normal, as in the S_C* phase, while (*c*) the helix axis in the S_{X_3} phase is parallel to the layer, similar to the TGB phase.

a blue reflection colour when it is prepared from the homogeneously aligned S_{X_1}, but no colour can be recognized when it is generated from the homeotropically aligned S_{X_1}. This means that the helical twisting of molecules takes place along a layer [see Fig. 3(*c*)], but not along the layer normal. The same result was obtained from the X-ray observations, as will be reported soon. This specific axis of helix along the layer is similar to that observed in the twisted grain boundary (TGB) phase.[6] The TGB_A (TGB_C) phase appears above the S_A (S_C*) phase. In this context, the S_{X_3} phase definitely differs from the normal TGB phase.

Finally we considered the origin of the helices. Two reasons can be inferred. One is due to the conformational chirality. This is based on the ground-state conformation in which the planes of the two aromatic rings joined by an ester (or amide) linkage are twisted.[7,8] If the conformational ground state is maintained in the liquid crystal state for any reason, the two benzylideneaniline groups in the mesogenic part may be twisted to each other like propera (see the chemical structure of $\mathbf{1}_n$). Two kinds of propera-like molecules with right- and left-handed twist are expected to be generated, and if the molecules are segregated with like twist sense and stack to form a layer, a twisting power arises in each segregated domain. As a second possibility, the twisting power can be induced from the dipole-dipole interaction.[9] Particularly in this ferroelectric system, the interaction may be significant and the helical twisting is considered to arise as a two-dimensional escape from the macroscopic polarization.[9,10] At present, we have no decisive data to select one of above reasons.

In conclusion, two types of helical structure are observed in two smectic phases consisting of banana-shaped achiral molecules. The local optical resolution occurs to form spatially resolved helices of both handednesses. This is the first observation of spontaneous generation of helical structures in achiral liquid crystalline systems.

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