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Heliconical-fluctuation-induced compensation point in the diluted cholesteric phase of mixtures containing the flexible dimer CB7CB

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(Dated: February 21, 2022)

We show experimentally and theoretically that the heliconical fluctuations that develop in a cholesteric phase (Ch) close to a transition to a chiral twist-bend nematic phase (N_{TB}) may lead to the appearance of a compensation point. At this point, the equilibrium twist of the cholesteric phase vanishes and changes sign. Mixtures of the flexible dimer CB7CB and the rod-like molecules 8CB or 5CB, doped with a small amount of the chiral molecules R811, S2011, CC or CB15, are used in experiments to determine the conditions for the appearance of a compensation point.

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I. INTRODUCTION

By doping a nematic phase with a small amount of a chiral molecule, one obtains a cholesteric phase in which the director $\vec{n}$ spontaneously rotates along a space direction called the helical axis [1]. In the structure at equilibrium, the director is perpendicular to the helical axis and turns 2π radians over a distance P called the helical pitch, corresponding to an equilibrium twist $q = 2\pi/P$. In most of the diluted cholesteric mixtures, the equilibrium twist does not change significantly with temperature. In this context,"diluted" means that the concentration of chiral molecules does not exceed a few percent by weight.

There are, however, exceptions to this situation, for instance when the liquid crystal (LC) presents a transition to a smectic A phase in which the molecules arrange in parallel layers. In that case, the pitch diverges at the transition when it is second order [2–7]. According to Alben [8] this divergence is due to the divergence of the twist elastic constant K_2 that is known to diverge as the coherence length ξ (by assuming that the coherence lengths parallel and perpendicular to the director are equal) [9–12]. Physically, this divergence is due to the deformation of the cybotactic groups which are transient domains of size ξ of smectic layerlike ordering [13]. It is remarkable to note that these groups have been experimentally observed only recently by electron microscopy in frozen samples [14]. It must be emphasized that this behavior is independent of the chemical nature of the chiral molecule used to dope the LC. Another exception occurs when the mixture has a compensation point at which the pitch diverges and changes sign. This situation is rather rare in diluted mixtures and crucially depends on the chemical nature of the chiral dopant as it results from particular interactions (steric, electric, etc.) between the LC molecules and the chiral dopant. One example is given in Ref. [15] where the LC used is the CCN-37 (4α,4'α-propylheptyl-1α,1'α-bicychlohexyl-4β-carbonitrile) and the chiral dopant is the cholesteryl chloride (CC), a molecule known to give a compensation point when it is mixed at high concentration with several usual LC such as 8CB (4-n-octyl-4'-cyanobiphenyl), 8OCB (4-n-octyloxy-4'-cyanobiphenyl) or MBBA (N-(4-methoxybenzylidene)-4-butylaniline) [16]. Another example was recently found by one of us (PO) in a mixture of a flexible dimer CB7CB (see below) and a rodlike molecule (8CB) doped with a very small amount of the chiral molecule R811 [17]. In this mixture, a surprising compensation point appeared in the vicinity of the twist-bend nematic phase (N_{TB}), contrasting with previous studies only mentioning a divergence of the pitch at the transition [18]. We recall that in the N_{TB} phase, the bent-core molecules spontaneously arrange into a doubly degenerate heliconical structure at a nanometer scale (for a review, see Ref. [19]).

In this paper, we determine under which experimental conditions such a compensation point occurs close to the N_{TB} phase and we suggest that this phenomenon is closely linked to the presence of cybotactic groups of the N_{TB} phase (Sec. II). To reinforce this hypothesis, a qualitative model is presented (Sec. III). Conclusions and perspectives are drawn in Sec. IV.

II. EXPERIMENTAL SECTION

The LC used is the flexible dimer CB7CB (1",7"-bis(4-cyanobiphenyl-4'-yl)heptane). It was purchased from Synthon (Germany) and used without further purification. In this molecule, the spacer between the

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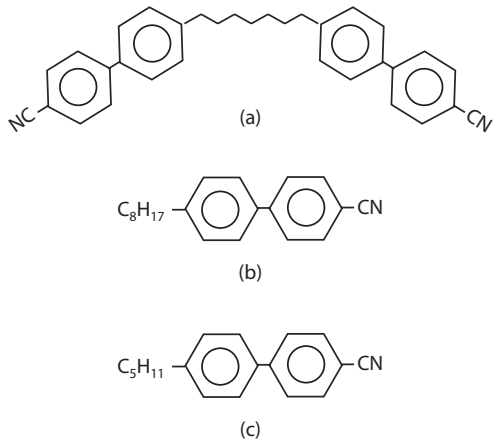

FIG. 1. Liquid crystals used: (a) CB7CB; (b) 8CB; (c) 5CB

two cyanobiphenyl (CB) groups contains an odd number of carbons (7) resulting in a bent-shaped molecule (Fig. 1(a)). This molecule is not chiral. Because of its shape, this LC has a phase transition between an uniaxial nematic and a twist-bend nematic phase at $T_{\mathrm{NB}} \approx 103.1\,°\mathrm{C}$. The nematic phase melts at $T_{\mathrm{NI}} \approx 115.5\,°\mathrm{C}$. By mixing CB7CB with a rod-like molecule such as 8CB (4-n-octyl-4'-cyanobiphenyl, Fig. 1(b)) or 5CB (4-n-pentyl-4'-cyanobiphenyl, Fig. 1(c)) it is possible to decrease both T_{NB} and T_{NI} while increasing the domain of existence of the nematic phase. In practice, we used the following mixtures: CB7CB+50 wt% 8CB (M1), CB7CB+37.5 wt% 8CB (M2), CB7CB+25 wt% 8CB (M3), CB7CB+12.5 wt% 8CB (M4) and CB7CB+50 wt% 5CB (M5) which all exhibit a transition from N to $\mathrm{N_{TB}}$ phases. 5CB was purchased from Merck (Germany) and 8CB from Synthon (Germany) and were used without further purification. The transition temperatures of the mixtures M1-M4 were measured between two bare glass plates in a Mettler oven FP82 and are reported in Fig. 2. For the mixture M5, we measured $T_{\mathrm{NB}} = 24.5°\mathrm{C}$ and $T_{\mathrm{NI}} = 59°\mathrm{C}$. These data are in good agreement with the phase diagrams of the mixtures CB7CB+8CB and CB7CB+5CB given in Ref. [20] and Ref. [21], respectively. Note that T_{NI} is here the temperature at which the first droplets of isotropic liquid nucleate upon heating (solidus temperature) and T_{NB} the temperature at which the first domains of $\mathrm{N_{TB}}$ phase nucleate upon cooling (liquidus temperature).

A. Materials

The chiral molecules used were R811 (R-(+)-octan-2-yl 4-((4-(hexyloxy)benzoyl)oxy) benzoate, Fig. 3(a)), CB15 (R-(+)-4'-(2-methylbutyl)-[1,1'-biphenyl]-4-carbonitrile, Fig. 3(b)), S2011 (S-(−)-4-(3,5-difluoro-4-(octan-2-yloxy)phenyl-4'-propyl-1,1'-bi(cyclohexane), Fig. 3(c)) and CC (cholesteryl chloride, Fig. 3(d)). All were purchased from Merck (Germany) and used as received.

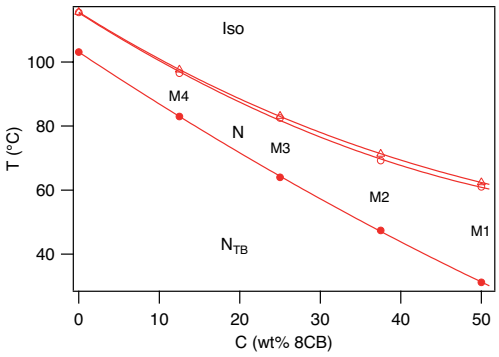

FIG. 2. Phase diagram of the mixture CB7CB+8CB. The mixtures M1-M4 are indicated on the graph. Open circles: T_{NI} (solidus temperature); Solid circles: T_{NB} (liquidus temperature). The open triangles give the temperature at which the last germs of nematic phase disappear upon heating (liquidus temperature). Solid lines are just guides for the eye.

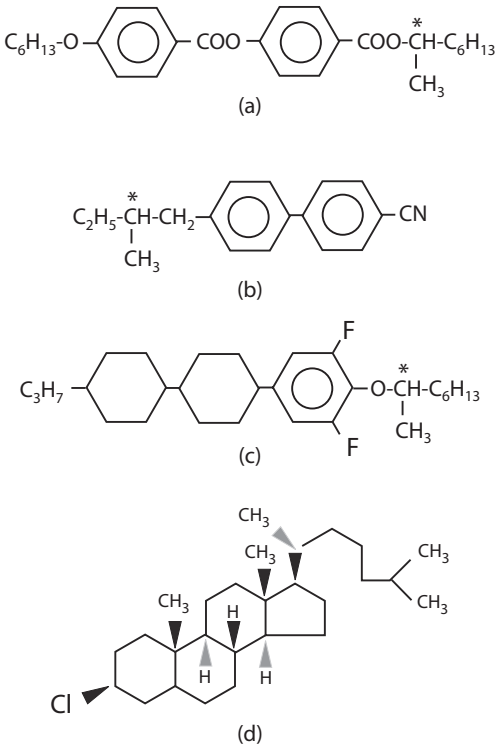

FIG. 3. Chiral dopant used: (a) R811; (b) CB15; (c) S2011; (d) CC

The first two (R811 and CB15) are known to give right-handed cholesteric phase, while the last two (S2011 and CC) give left-handed cholesteric phases [22].

B. Experimental setup and sample preparation

All observations were made with a Leica Laborlux 12 Pol Microscope equipped with a Guppy F-503 CMOS camera. The samples were prepared between indium tin

oxide (ITO) coated glass slides. Their thickness was fixed thanks to Nickel wires or silica micro-beads used as a spacer and was measured with an Ocean Optics USB2000 spectrometer. It ranges between 2 and 15 µm depending on the concentration of chiral molecules in the mixture. A home-made oven was used to fix the temperature of the samples. The temperature was regulated to within ±0.01 °C thanks to an ATNE ATSR100 PID temperature controller. The polyimide Nissan 0825 was used to prepare the plates treated for planar unidirectional anchoring according to the protocole described in Ref. [23]. A thin polymercaptan layer was used to obtain a planar sliding anchoring according to the protocole described in Ref. [24].

C. Pitch measurements

In practice, the classical Cano wedge technique [1] cannot be used to measure the pitch close to a N_{TB} phase transition. The main reason is due to the existence of a band instability of the texture [17] that shifts the χ-lines from their usual equilibrium position in $d = P/4; 3P/4; 5P/4...$ (with d the sample thickness), making impossible a precise measurement of the pitch. Another limitation comes from the large viscosity of the mixtures containing CB7CB leading to equilibration times of the texture that can exceed one day.

For these reasons, we chose another method consisting of measuring the rotatory power of thin samples sandwiched between a plate treated for planar unidirectional anchoring and a second one treated for planar sliding anchoring. The details of this measurement are given in Ref. [17]. In short, the sample is placed under the microscope and is illuminated with a polarized light beam whose incident polarization is parallel to the director on the bottom plate treated for planar unidirectional anchoring. The rotatory power is determined by measuring for which angle between the polarizer and the analyzer the transmitted intensity I_{tr} is maximum. From this angle, the pitch is determined by using the Ong formula [25, 26] that allows to calculate I_{tr} provided that the birefringence is known. Note that using this formula is necessary, in particular at high temperature, when the Mauguin condition for the adiabatic rotation of the light polarization is no longer fulfilled. For the mixtures M1, we used the birefringence data given in Ref. [17]. For the other mixtures, the birefringence was measured using a Berek rotating compensator following the protocole described in Ref. [17]. The major advantage of this technique is that the measurements are very fast because the samples equilibrate within a few minutes after each temperature change.

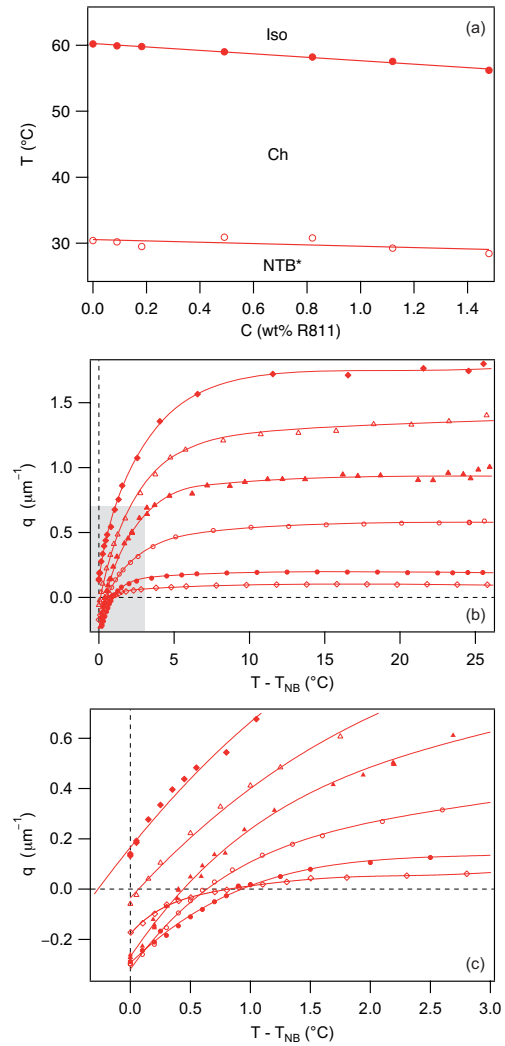

FIG. 4. (a) Phase diagram of the mixture M1+R811. (b) Equilibrium twist q as a function of the temperature shift $T - T_{NB}$ for the mixture M1 doped with (from bottom to top) 0.09 (empty diamonds), 0.181 (solid circles, data taken from Ref. [17]), 0.49 (empty circles), 0.82 (solid triangles), 1.12 (empty triangles) and 1.48 wt% (full diamonds) of R811. (c) Zoom on the data shown in (a) inside the rectangle in light gray. The solid lines are just guides for the eye.

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D. results

We first measured the equilibrium twist q of the mixture M1 doped with increasing concentrations of R811. The phase diagram of this mixture and typical curves are shown in Fig. 4. As expected with R811, we observe that $q > 0$ (right-handed cholesteric) and is approximately constant far from the transition to the N_{TB} phase. In this regime, q is proportional to the concentration of R811 as shown in Fig. 5(a). From this figure, the helical twist power –defined to be HTP= $1/PC$ where C is the concentration by weight of the chiral molecule– can be calculated at $T - T_{NB} = 30\,°C$: $HTP_{R811} =$

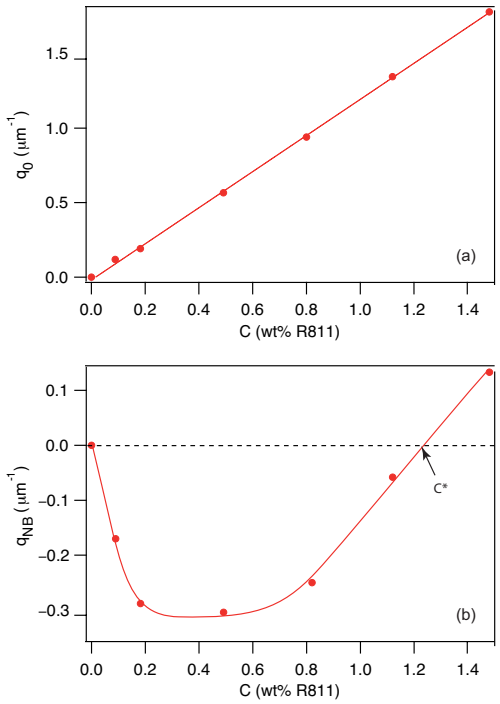

FIG. 5. Equilibrium twist measured at $T - T_{\mathrm{NB}} = 30\,^{\circ}\mathrm{C}$ (denoted by q_0) (a) and at $T = T_{\mathrm{NB}}$ (denoted by q_{NB}) (b) as a function of the concentration of R811 in the M1 mixture. The solid line in (a) is the best linear fit of the data. The solid line in (b) is just a guide for the eye.

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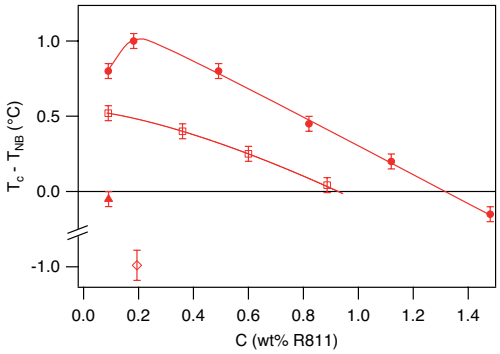

FIG. 6. Temperature difference $T_c - T_{\mathrm{NB}}$ as a function of the concentration of R811 for the mixture M1 (solid circles), M2 (empty squares), M3 (solid triangle) and M4 (empty diamond). The negative values of $T_c - T_{\mathrm{NB}}$ for the mixtures M1, M3 and M4 were obtained by extrapolating to 0 the $q(T)$ curves.

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$19.2\,\mu\mathrm{m}^{-1}\,\mathrm{wt}\%^{-1}$. This value is pretty large in comparison to that found with usual LC such as cynanobiphenyls (around $13\,\mu\mathrm{m}^{-1}\,\mathrm{wt}\%^{-1}$ [22]). This is due to the large molar mass of the CB7CB as one immediately realizes by calculating the HTP in $\mu\mathrm{m}^{-1}\mathrm{mole}\%^{-1}$. In these units, the HTP have similar values in all the LC. Much more interesting is the observation of a compensation point near

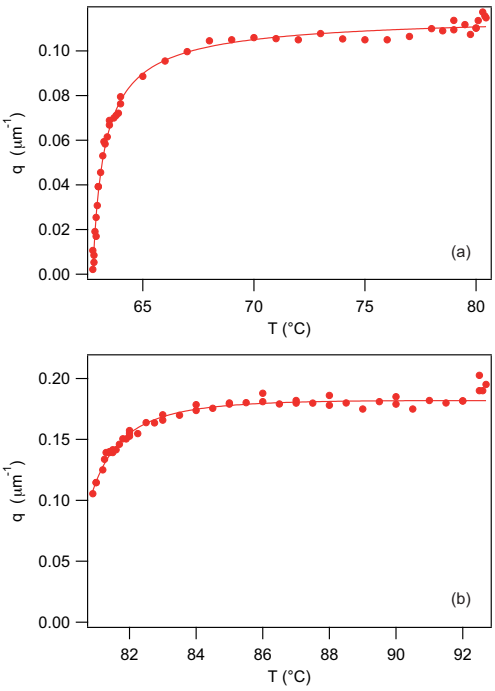

FIG. 7. Equilibrium twist as a function of temperature for the mixtures M3 + 0.091 wt% R811 (a) and M4 + 0.194 wt%R811 (b).

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T_{NB} which disappears above a critical concentration $C^{\star}$ close to 1.25 wt% (Fig. 5(b)). This is also visible in Fig. 6 in which the temperature difference $T_c - T_{\mathrm{NB}}$ is plotted as a function of C, by denoting by T_c the compensation temperature. Another interesting point is that the twist has always a finite value at T_{NB} as shown in Fig. 5(b).

Chiral dopant	HTP ($\mu\mathrm{m}^{-1}\,\mathrm{wt}\%^{-1}$)
R811	19.2
CB15	10.8
S2011	-15.1
CC	-3.44

TABLE I. HTP of the chiral dopants measured at $T - T_{\mathrm{NB}} = 30\,^{\circ}\mathrm{C}$ in the mixture M1.

We then performed similar measurements with the mixtures M2, M3 and M4. With the mixture M2, we observed again the existence of a compensation point at small concentration of R811. For this mixture, we found that $C^{\star} \approx 0.93\,\mathrm{wt}\%$ as shown in Fig. 6. This is less than the value found with the mixture M1. Finally, we observed that the compensation point disappears in mixtures M3 and M4 (Fig. 7). In that case, q is positive whatever the temperature and the concentration of R811. In addition, the decrease of the equilibrium twist q is much less important when approaching from the $\mathrm{N_{TB}}$ phase in mixture M4 than in mixture M3. These results show that the larger the temperature interval in which the cholesteric phase exists, the larger is the varia-

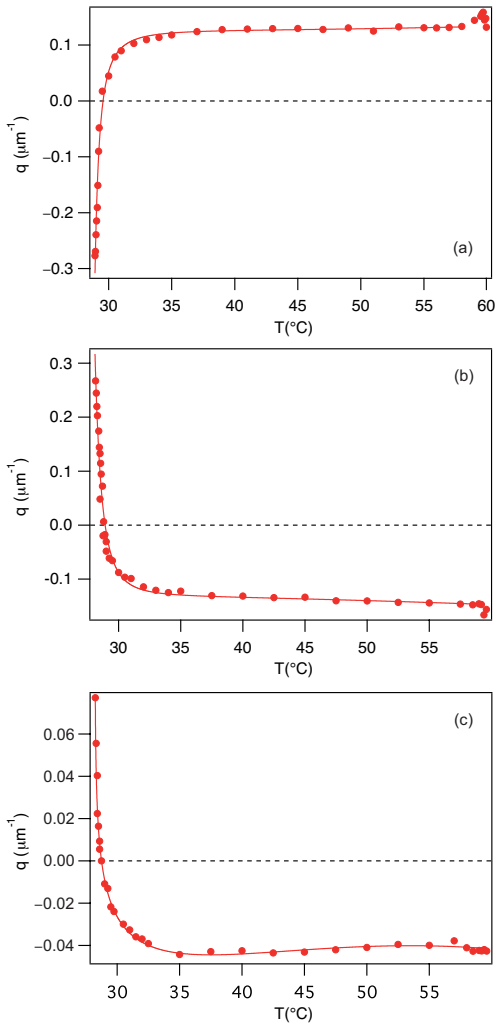

FIG. 8. Equilibrium twist as a function of temperature for the mixture M1 doped with 0.19 wt% CB15 (a), 0.147 wt% S2011 and 0.185 wt% CC (c).

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tion of the equilibrium twist when approaching from the N_{TB} phase. In particular, the cholesteric phase must exist over a wide enough temperature interval to observe a compensation point in the vicinity of the N_{TB} phase. This behavior is clearly related to the first order character of the Ch-to-N_{TB} phase transition which is known to decrease when the temperature interval $T_{NI}-T_{NB}$ increases. This is indeed confirmed by latent heat measurements as those reported in Ref. [21] for the mixture CB7CB+5CB. In that case, the latent heat decreases by a factor of 4 with respect to the pure CB7CB for a concentration of 5CB close to 40 % by weight.

The next question to solve was to determine whether the existence of the compensation point depends on the chemical nature of the chiral molecules. This is clearly the case with the LC CCN-37 for which a compensation point is observed with the CC –but not with R811. This is shown in Ref. [15]. Is it similar with the mixture

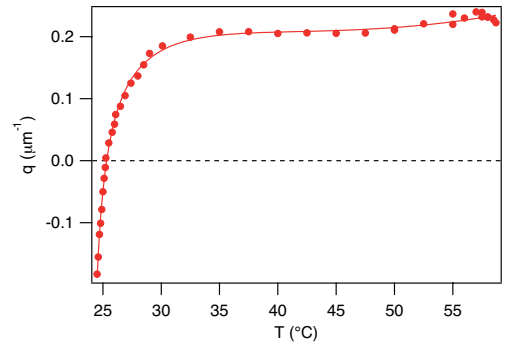

FIG. 9. Equilibrium twist as a function of temperature for the mixture M5 doped with 0.257 wt% R811.

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M1? To address this question, we doped the mixture M1 with small amounts of the chiral molecules CB15, S2011 and CC. With all of the mixtures, we observed the same behavior as with R811, i.e. the existence of a compensation point near the N_{TB} phase and a plateau at high temperature. Typical curves are shown in Fig. 8. From these curves the HTP of each chiral dopant was deduced. Their values at $T-T_{NB}=30\,°C$ are given in Table 1. As expected, the HTP of R811 and CB15 is positive, while the HTP of S2011 and CC is negative. In all cases, we also observe that the HTP of these chiral dopants is typically 1.5 times larger than in usual nematic LC when the percentages are given in wt%. This study shows an important result, namely that the existence of the compensation point is independent of the chemical nature of the chiral dopant. As a consequence, the compensation point is not due to specific interactions between the LC and the chiral molecules, but rather to a pretransitional effect when the N_{TB} phase is approached.

To confirm this point, we also tested the role of the rod-like molecule used. We replaced 8CB by 5CB and prepared a sample of the mixture M5 doped with 0.2 wt% of R811. With this mixture, we again observed a compensation point close to the N_{TB} phase as can be seen in Fig. 9. This result confirms that molecules other than 8CB can be used and that only the presence of a N_{TB} phase is necessary to observe a compensation, provided that the phase transition is weakly enough first order.

III. QUALITATIVE MODEL

Our observations show that the existence of a compensation point is due to the presence of a N_{TB} phase. This observation contrasts with what is observed at the cholesteric-smectic A phase transition where q vanishes –but does not change sign. In the latter case, the deformation of the cybotactic groups of lamellar phase is responsible for the pitch divergence. By analogy, one could think that the deformation of the cybotactic groups of N_{TB} phase could play the same role because of their

lamellar-like structure. This interpretation was indeed proposed by the authors of Ref. [18] to explain the large increase of the pitch measured in their mixtures at large concentration of chiral dopants. This interpretation is certainly partly correct, but fails to explain the twist reversal at low concentration of chiral molecules. Note that this analogy with the N-to-SmA transition has also been proposed to explain the increase of the bend constant K_3 that is observed near the N_{TB} phase [20, 23, 27].

Contrary to the case of the Ch-to-SmA phase transition, the twist constant K_2 does not diverge at the compensation temperature in the present mixtures [17]. For this reason the explanation for the divergence of the pitch must be different. Major differences indeed exist between cybotactic groups of SmA and N_{TB} phases:

- First, the cybotactic groups of the N_{TB} phase remain locally nematic and can be more easily twisted than those of the SmA phase in which a true lamellar structure exists. The twist of the cholesteric helix deforms the pseudo-layered director field inside the N_{TB} groups. This tends to untwist the helix, similar to the SmA transition. However, this effect cannot lead to a complete compensation without the divergence of K_2.

- Second, the N_{TB} groups are chiral, because the heliconical arrangement of the molecules inside is twisted either to the right or to the left. In cholesteric LC, one of the two chiralities is favored. In the following, we show qualitatively that this imbalance between the two enantiomeric configurations is fundamental and can lead to an inversion point, because forming heliconical N_{TB} groups with a favorable twist becomes easier if the cholesteric helix is twisted in the opposite direction.

For this purpose, we calculated the elastic energy stored inside a deformed cybotactic group. This calculation is qualitative but could serve as the starting point for a more complete theory.

The elastic free energy per unit volume of the cholesteric phase is given by

$$F = \frac{1}{2}\,K_1\,(\vec{\nabla}\cdot\vec{n})^2 + \frac{1}{2}\,K_2\,(\vec{n}\cdot\vec{\nabla}\times\vec{n}+q_0)^2 + \frac{1}{2}\,K_3\,(\vec{n}\times\vec{\nabla}\times\vec{n})^2 \tag{1}$$

In this expression, q_0 is the bare spontaneous twist, and K_1, K_2 and K_3 are the bare splay, twist and bend (flexoelectricity renormalized [28]) elastic constants, not taking into account heliconical fluctuations.

The helical axis is taken along the z-axis, so that the director has components:

$$\vec{n} = \begin{pmatrix} \cos q\,z \\ \sin q\,z \\ 0 \end{pmatrix} = R(q\,z) \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \tag{2}$$

where $R(\Phi)$ is the matrix that rotates vectors by Φ around the z axis. Note that q may be different from q_0.

We then choose a particular form of the cybotactic group, namely we assume that the director takes the form

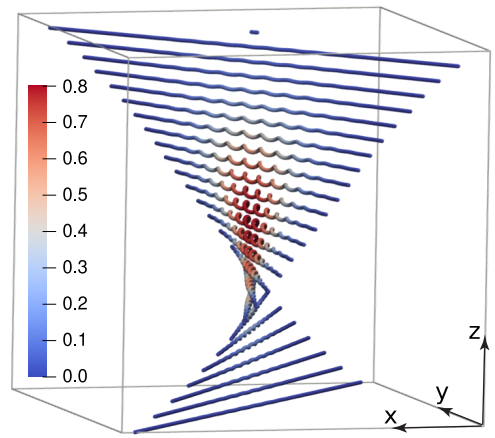

FIG. 10. Field lines of the director inside the cybotactic group defined by Eqs. (3)-(5). The color indicates the magnitude of angle θ in rad.

$$\vec{n} = R(q\,z) \begin{pmatrix} \cos\theta \\ \sin\theta\cos\phi \\ \sin\theta\sin\phi \end{pmatrix} \tag{3}$$

with

$$\theta = \theta_0\,\exp\left[-\frac{1}{2}\left(\frac{u^2+v^2}{\sigma^2} + \frac{z^2}{\sigma_z^2}\right)\right] \tag{4}$$

$$\phi = k\,u + \phi_0 \tag{5}$$

In this equation, θ_0 is the amplitude of the fluctuation, assumed to be small. σ and σ_z are the extent of the fluctuation perpendicular and parallel to the helicoidal axis z. k is the wave vector of the heliconical perturbation, which is large because the heliconical pitch is typically 10 nm [21]. u and v are the coordinates in the rotated frame, i.e.

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = R(q\,z) \begin{pmatrix} u \\ v \\ z \end{pmatrix} \tag{6}$$

The director field is represented in figure 10.

The elastic free energy F is expanded up to second order in θ_0 and the excess free energy $\delta F = F - \frac{1}{2}\,K_2(q-q_0)^2$ is integrated over the full space. All the calculations are performed using Mathematica. After dividing by the volume of the cybotactic group $V = (2\pi)^{3/2}\sigma^2\sigma_z$, the average contribution of the cybotactic group to the free energy is found to be

$$\langle\delta F\rangle = \frac{\theta_0^2}{8\sqrt{2}}\left[q^2\left(\frac{K_1+K_2}{2}\,k^2\sigma^2 + K_3 - 2\,K_2\right) + q\left(2\,K_2\,q_0 + (3\,K_2 - K_1 - 2\,K_3)\,k\right) + \frac{K_1+K_2+2\,K_3}{2\,\sigma^2} + 2\,k\,(K_3\,k - 2\,K_2\,q_0)\right] \tag{7}$$

In this equation, a term proportional to $e^{-k^2\,\sigma^2}$ was neglected because the cybotactic group is assumed to extend over several heliconical wavelengths. To simplify, we also neglected the term in $\frac{\theta_0^2}{8\sqrt{2}}\frac{K_1+K_2}{2\sigma_z^2}$ by assuming that $\sigma_z \gg \sigma$, although this hypothesis is not really necessary in the rest of the discussion.

By adding back the mean field contribution $\frac{1}{2}\,K_2(q-q_0)^2$ and by minimizing $\langle F\rangle$ with respect to q, one obtains a renormalized equilibrium twist q up to order 2 in θ_0:

$$q = q_0 + \frac{\theta_0^2\,q_0}{8\sqrt{2}\,K_2}\Bigg(2\,(K_2-K_3)-(K_1+K_2)\,k^2\,\sigma^2 + (K_1-3\,K_2+2\,K_3)\,\frac{k}{q_0}\Bigg) \quad (8)$$

There are three terms in the parenthesis:

- The first one is constant and positive since K_3 is smaller than K_2 in the mixtures with CB7CB.

- The second one in $k^2\,\sigma^2$ is always negative. Its magnitude is greater than that of the first one whenever $K_1 > K_2$ and $k^2\,\sigma^2 > 1$. This term tends to decrease the equilibrium twist as observed experimentally and is all the more significant when σ is large. This is the case if the Ch-to-N_{TB} phase transition is weakly first order, in agreement with the experimental observations that show that a compensation point is only observed in the mixtures in which the latent heat of the Ch-to-N_{TB} phase transition is small enough.

- The third term in k/q_0 is more ambiguous. A priori, the prefactor $K_1-3K_2+2K_3$ is negative when $K_3 \ll K_{1,2}$ and $K_2 > K_1/3$. However, the sign of k/q_0 has to be determined because cybotactic groups with positive or negative k are possible. Although both chiralities would be equally probable in the nematic phase, the situation is clearly different in the cholesteric phase in which one type of groups is expected to dominate. Indeed, Eq. (7) shows that the odd term in k in the energy of the cybotactic group is

$$\langle\delta F_{\rm odd}\rangle = \frac{\theta_0^2\,k\,q_0}{8\sqrt{2}}\Bigg((3\,K_2-K_1-2\,K_3)\,\frac{q}{q_0}-4\,K_2\Bigg) \quad (9)$$

The parenthesis is negative when $\frac{q}{q_0} < \frac{4\,K_2}{3\,K_2-K_1-2\,K_3}$, which is indeed the case experimentally.

This expression shows that the energy is minimum if $k\,q_0 > 0$. That means that the groups with k of the same sign as q_0 are favorable. The immediate consequence is that the third term in the parenthesis of Eq. (8) is also negative and contributes to decreases q in absolute value. One interesting point is that this term is inversely proportional to q_0. For this reason, the smaller the concentration of chiral molecules, the greater $1/q_0$ and this term in absolute value. This could qualitatively explain why we only observe a compensation point in the most diluted mixtures. Note that all of our observations suggest that both the second and third terms play a role in the appearance of a compensation point. Indeed, the second one is important to explain the role played by the first-order character of the transition while the third one underlines the importance of the magnitude of q_0 (without this term one would always observe a compensation whatever the value of q_0, in contradiction with experiments).

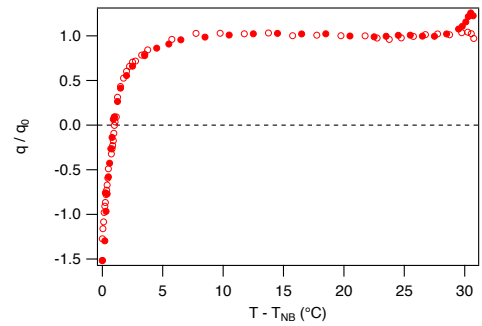

FIG. 11. Curves q/q_0 as a function of the temperature shift $T-T_{\rm NB}$ for the mixture M1 + 0.182 wt% R811 (solid circles) and the mixture M1 + 0.88 wt% CC (open circles). The concentrations of chiral molecules were chosen in order that q_0, here measured at 50 °C, was the same for the two mixtures and equal to 0.19 µm^{-1}. The curves superimpose despite the fact the two chiral molecules are very different and of opposite handedness.

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An attentive reader will note that the previous Eqs. (7) and (8) are only valid when the relative fraction of groups with a wavevector k of the same sign as q_0 is close to 1. This will be the case if q_0 is large enough in absolute value. However, these equations are inconsistent and must be modified in the limit $q_0 \to 0$, as one can see immediately from Eq. (8) that shows that $q \to$ constant $\neq 0$. In this limit, the linear term in k in these two equations must be weighted by a factor $\delta f = f^+ - f^-$ where f^+ (f^-) are the relative fractions of groups of wavevector k ($-k$) by taking k of the same sign as q_0. This factor is difficult to estimate here, but we can predict that, in the limit $q_0 \to 0$, q and δf should be proportional to q_0. In this way, the previous contradiction disappears since $q \to 0$ when $q_0 \to 0$, as expected for a nematic phase and in agreement with Fig. 5.

Taking this remark into account, we see in the end that the curve $q(T)$ must only depend on T and q_0. Indeed, Eq. (8) can be rewritten as

$$\frac{q}{q_0} = 1 - A(T) - B(T)\,\frac{\langle k\rangle(q_0,T)}{q_0} \quad (10)$$

where A and B are functions of T that only depend on the LC mixture.

From Eq. (10), two important predictions follow that can be verified experimentally:

- The first one is that, for a given LC mixture, the curve $q(T)$ must only depend on q_0, independently of the chiral molecule chosen. More precisely, the curve q/q_0 vs. $T-T_{\rm NB}$ (where q_0 is the value of q measured on the plateau at high temperature, for instance at $T-T_{\rm NB} =$ 30 °C for the mixture M1) must be the same for all the

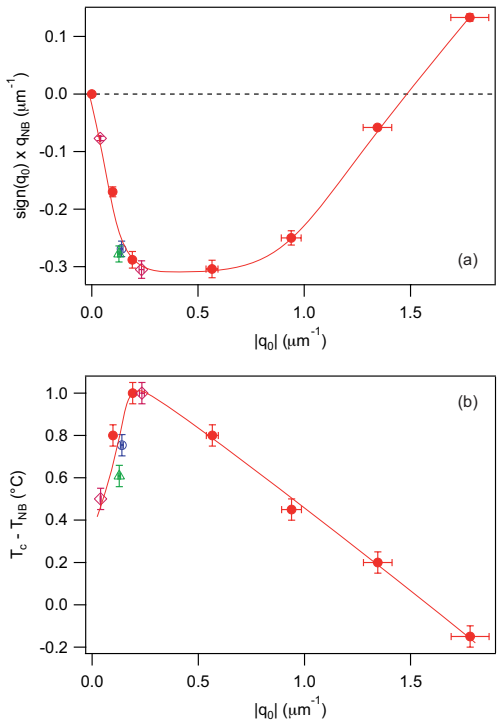

FIG. 12. Curves sign $(q_0) \times q_{\rm NB}$ versus $|q_0|$ (a) and $T_c - T_{\rm NB}$ versus $|q_0|$ (b) for all the samples prepared with the M1 mixture. The solid circles have been measured with R811, the empty circle with S2011, the empty triangle with CB15 and the empty diamonds with CC. In each graph all the points fall on the same master curve within experimental errors. The solid lines are just guides for the eye.

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chiral molecules provided that q_0 is the same in absolute value. To check this point, we compared a mixture of M1 + R811 with a mixture of M1 + CC. These two chiral molecules were chosen on purpose because they are chemically very different, as can be seen in Fig. 3, and of opposite handedness. We prepared a mixture of M1 + 0.88 wt% CC. This concentration was chosen in order that q_0 be the same in absolute value as the one of the mixture M1 + 0.182 wt% R811 (see Fig. 4(a)). We then measured the curve $q(T)$ for this new mixture and we reported on the same graph in Fig. 11 the curves q/q_0 as a function of $T - T_{\rm NB}$ for the two mixtures. Remarkably, one observes that the two curves are very similar and superimpose as predicted by the model.

- The second prediction is that, for a given LC mixture, the curves $\mathrm{sign}(q_0) \times q_{\rm NB}$ versus $|q_0|$ and $T_c - T_{\rm NB}$ versus $|q_0|$ must be the same for all the chiral molecules chosen. This is indeed the case for the mixture M1 as can be seen in Fig. 12 where all the experimental points fall on the same master curves.

All of these observations confirm that the heliconical fluctuations (or cybotactic groups of $\mathrm{N_{TB}}$ phase) are responsible for the pitch variation near the $\mathrm{N_{TB}}$ phase.

Finally, the influence of the $\mathrm{N_{TB}}$ fluctuations on K_2 can also be qualitatively assessed. The renormalized K_2 is indeed given by

$$\bar{K}_2 = \frac{\partial^2 \langle F \rangle}{\partial q^2} = K_2 + \frac{\theta_0^2}{8\sqrt{2}} \left(2\,K_3 - 4\,K_2 + (K_1 + K_2)\,k^2\sigma^2 \right) \quad (11)$$

This formula shows that the measured twist constant $\bar{K}_2$ increases when approaching $T_{\rm NB}$ from above, but does not diverge as long as $k\,\sigma$ remains finite, which is the case when the transition is first order. This was indeed observed experimentally [17].

In the same way, the two other elastic constants should be renormalized by the presence of the cybotactic groups. This is clearly visible for K_3 that is observed to increase in the same interval of temperature as the pitch when approaching from $T_{\rm NB}$ [20, 23, 27, 29].

IV. CONCLUSION

We have shown experimentally that the compensation point that occurs near the $\mathrm{N_{TB}}$ phase in the diluted cholesteric mixtures containing the flexible dimer CB7CB is not accidental, but mainly due to the particular elastic properties of the cybotactic groups of $\mathrm{N_{TB}}$ phase present in the cholesteric phase. In particular, the choice of the chiral molecule is not crucial, only counting its HTP measured at high temperature in the absence of cybotactic groups.

Particular conditions are nonetheless required to observe a compensation.

- First, the phase transition must be weakly enough first order in order for the cybotactic groups to be big enough. This condition is realized by mixing CB7CB with a rodlike molecule like 8CB or 5CB in order to increase the temperature interval in which the cholesteric phase exists. From this point of view, the situation is the same as in mixtures with a nematic-to-smectic A (NA) phase transition. One example is the mixture 8CB + 10CB in which the NA phase transition passes from first to second order when the temperature interval in which the nematic phase exists becomes larger than 1.4 °C typically [9, 30]. It would be interesting to precisely measure the latent heat of the $\mathrm{N_{TB}}$-to-N phase transition in the mixture CB7CB + 8CB to check whether it exists a similar tricritical point. This could be the case if one refers to the similar mixture CB7CB + 5CB in which such a point seems to exist for a concentration of 60 wt% of 5CB (value obtained by extrapolating to 0 the latent heat data given in Ref. [21]).

- Second, the spontaneous twist q_0 must be very small in absolute value, which certainly explains why the compensation was not observed before, the vast majority of the papers dealing with the optical properties of the heliconical structure induced by an electric field at large q_0 (several µm^{-1} to observe Bragg diffraction and mirrorless lasing in the visible spectrum) [31].

In the future, it would be important to improve the theoretical model. Indeed, our model is very qualitative because the cybotactic groups are localized in space and transient, and because different forms than that given in Eqs. (3)–(5) exist. In addition, our model does not allow to calculate the wavenumber k of the heliconical modulation, nor its amplitude θ. The size of the cybotactic groups is also unknown. One could be tempted to calculate k and σ by minimizing our energy (7) as a function of k and σ. This procedure is possible but leads to a value of k that is inversely proportional to K_3. This result is obviously incorrect since k remains finite at the transition to the N_{TB} phase when K_3 tends to 0 [32]. This is due to the fact that we have omitted in our calculation the fourth-order elastic term introduced by Dozov in the expression of the elastic energy to calculate k and θ [32]. So our calculation is only consistent by assuming that k and θ are fixed and probably of the same order of magnitude as in the N_{TB} phase at the phase transition. The next step would thus to take into account this term and to integrate on all the possible Fourier modes of the heliconical fluctuations. Such a calculation is out of the scope of this paper but is planned for future work.

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