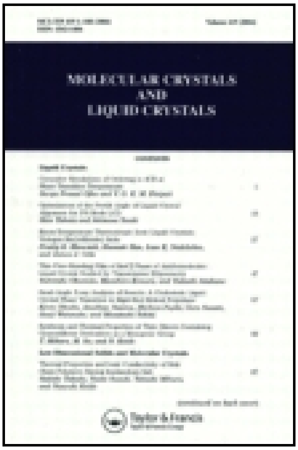

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Material Parameters and Intrinsic Optical Bistability in Room Temperature Nematics RO-TN-200, -201, -403, E7, m_1, and m_3

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Material Parameters and Intrinsic Optical Bistability in Room Temperature Nematics RO-TN-200, -201, -403, E7, m_1, and m_3

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New measurements are reported of the elastic constants and refractive indices of the room temperature nematics RO-TN-200, -201, -403 and E7. The new measured material parameters show that the purely optical field induced first-order Freedericksz transition can not be attained by these materials. However, the first-order Freedericksz transition can be enhanced in these nematics by an external magnetic field. We also report two new nematic mixtures for which the purely optical field induced first-order Freedericksz transition can be attained.

Keywords: liquid crystal, optical bistability, Freedericksz transition, phase transition

The electromagnetic field induced Freedericksz transition (molecular reorientation) in nematic liquid crystals (NLCs) has been studied extensively in the last twenty years. But since the first observation made by Freedericksz in 1927, all the observed Freedericksz transitions in NLCs are second order.[1] In the last few years, a great deal of attention has been focused on the optical field induced Freedericksz transition in a homeotropic oriented NLC cell. It has been shown that the reorientation torque produced by a cw optical field on NLCs

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can result in an extremely strong collective molecular reorientation leading to large associated nonlinear effects.[2] Recently, we obtained the exact solution for describing the NLC orientation and found that certain existing NLCs can have first-order and intrinsic optical bistable (OB) transitions in which increasing optical field intensity results in discontinuous changes in the LC orientation.[3,4] The optical field induced first-order transition hence provides a possibility for the first observation of a first-order Freedericksz transition in NLCs. This form of intrinsic OB does not use a resonant optical cavity and is a viable candidate for the achievement of room temperature, low power and externally controllable optical switches.

Our early study showed that without an additional magnetic or electric field, the criterion for the existence of the intrinsic optical bistability in NLCs is given by $B_o = (k_{11}/k_{33} + 9n_o^2/4n_e^2 - 9/4)/4 < 0$, where k_{11} and k_{33} are the splay and bend elastic constants, n_o and n_e are the ordinary and extraordinary indices of refraction.[3,4] We also showed that using an additional magnetic or electric field, OB can always be enhanced or suppressed and hence can be seen in all existing nematics at a low laser power.[5] The enhancement of the first-order transition by an additional bias magnetic field has been recently observed experimentally.[6] This is the first experimental observation of the first-order Freedericksz transition in NLCs. For most of the existing NLCs, the criterion for the purely optical field induced first-order Freedericksz transition is not satisfied and the transition is second order. However, by examining the material parameters of a few hundred existing NLCs, we found that OB can occur in the following four room temperature NLC mixtures: RO-TN-200, RO-TN-201, RO-TN-403 (from Hoffmann-La Roche) and E7 (from British Drug House), as well as in the high temperature single component nematic PAA (p-azoxyanisole).[5,7] Table I summarizes the OB predictions and the material parameters of these four room temperature NLCs.

Since reliable methods to determine especially the twist (k_{22}) and bend (k_{33}) elastic constants were developed only during the last few years, many of the few elastic data published before 1979 are rather ambiguous.[11] Therefore, and because the elastic constants of the above nematics were measured in 1978,[8] all of them are remeasured in F. Hoffmann-La Roche Co. using the methods described in Ref. 11. The most straightforward method to determine elastic constants is via the observation of threshold fields in different types of Freedericksz transitions. Both the splay and bend elastic constants can be determined in the same cell provided a very low bias tilt surface

TABLE I

Summary of the old material parameters and predictions on the intrinsic optical bistability in room temperature NLCs RO-TN-200, -201, -403 and E7. $B_0 = (k_{11}/k_{33} + 9n_o^2/4n_e^2 - 9/4)/4$, I_{th} and I'_{th} are the rising and falling threshold intensities. The threshold intensity in W/cm^2 is calculated for a 250 μm thick-cell. The elastic constants are in $10^{-7}dyne$

NLC	k_{11}	k_{22}	k_{33}	n_o	n_e	B_o	Order	I_{th}	I'_{th}/I_{th}
RO-TN-200	8.80	8.35	19.00	1.5345	1.8100	−0.042	First	209	0.986
RO-TN-201	13.03	13.30	25.40	1.5295	1.8170	−0.036	First	270	0.990
RO-TN-403	12.60	10.80	23.10	1.5235	1.7810	−0.015	First	268	0.998
E7	10.70	10.00	20.70	1.5222	1.7462	−0.006	First	268	0.999

alignment can be prepared. Direct threshold measurements to determine the bend elastic constant have to be preformed in cells with homeotropic surface alignment. However, homeotropic boundaries are more difficult to prepare than parallel aligned surface considering the high precision and uniformity required. Therefore, the bend elastic constant is normally determined in parallel aligned cells using either the initial slope of the field-dependent deformation-sensitive quantity used (approximation for small angles of deformation) or the dependence of this quantity over the whole range of field-induced deformation (numerical fitting required). The quantity used to monitor the status of the deformation is usually either the induced birefringence or the capacitance. Since a small angle deformation approximation was used for determining k_{33} of the above nematics when they were first published,[8] errors up to 30% occurred. As a consequence, and because k_{22} was measured in twist cells from k_{11}, and k_{33} and the threshold voltage V_{th} using $V_{th} \propto [k_{11} + (k_{33} - 2k_{22})]$, also the k_{22} data became erroneous.

The remeasured elastic constants and refractive indices of nematic mixtures RO-TN-200, -201, -403 and E7 are summarized in Table II. Table II also includes the new predictions on the OB for the four room temperature NLCs using the new material parameters. The new results lead to $B_o > 0$ for all four NLCs. Consequently the purely optical field induced Freedericksz transition is second order and hence no optical bistability can be expected in RO-TN-200, -201, -403, and E7.

All NLCs in Table II exhibit a small but positive value B_o. Because of the tendency of aromatic rings to lead to low elastic ratios k_{33}/k_{11} while simultaneously exhibiting large optical anisotropies, it is difficult to find NLCs fulfilling the optical bistability criterion B_o. De Jeu and Claassen who investigated a homogeneous series of nonpolar azoxybenzenes found that k_{33}/k_{11} decreases with increasing chain

TABLE II

Summary of the remeasured material parameters and consequent predictions of the intrinsic optical bistability in the NLCs listed in Table I. The threshold intensity in W/cm^2 is calculated for a 250 μm thick-cell. The elastic constants are in $10^{-7}dyne$. The measuring temperature is 22°C

NLC	k_{11}	k_{22}	k_{33}	n_o	n_e	B_o	Order	I_{th}
RO-TN-200	9.21	4.74	14.83	1.534	1.795	0.004	Second	170
RO-TN-201	12.79	6.11	19.61	1.529	1.812	0.001	Second	211
RO-TN-403	12.68	6.43	19.88	1.524	1.770	0.014	Second	239
E7	11.09	5.82	15.97	1.522	1.746	0.038	Second	207

length.[23] An analogous behavior was reported for polar phenylcyclothexanes (PCHs) by Schadt, Baur and Meier.[13] Recently Schadt and Gerber[22] found that k_{33}/k_{11} of a liquid crystal class is strongly affected by its polarity as well as by the type of ring structures used in the rigid part of the molecules. From the calculations of Priest[14] and Straley[15] who included higher order terms in the intermolecular mean-field potential of the Onsager hard rod model, one concluded that k_{33}/k_{11} increases in NLCs with increasing length to width ratio L/d of the NLC.[16-18] Sun and Klemen recently found that in a typical main-chain polymer belonging to a polyester series, k_{11} is very large compared to convential NLCs, while k_{22} and k_{33} have more conventional values.[21] However, experiments performed in conventional NLCs with dielectrically and structurally distinct but comparable differences indicate that geometrical considerations alone are inadequate to predict the important elastic ratios of NLCs,[22] molecular-specific interactions have to be taken into account. Recently, it has been found that a number of new polar cyanoalkenyl NLC classes with a double bond in their side chains exhibit interesting elastic properties, i.e., the ratio k_{33}/k_{11} strongly depends on the position of the double bond.[23] Consequently the nematic mixtures using appropriate NLCs show large values of k_{33}/k_{11} as well as low ratios n_o/n_e.[23] The following two mixtures $m_3 = (1d_3CP,\ 0d_3CP)$ and $m_5 = (1d_3CAP,\ 0d_3CAP)$ were found to exhibit $k_{33}/k_{11} = 2.97$ and 2.75 respectively at 22°C.[23] As a result, the purely optical field induced first-order Freedericksz transition should for the first time become manifest at room temperature when using these two nematic mixtures (see Table III). Therefore it is reasonable to expect that more NLC mixtures can be designed exhibiting negative valued B_o thus also leading to purely optical field induced first-order Freedericksz transitions.

Recently, we have shown that[5] when using an additional magnetic field **H** or electric field **E** directed along the optical field propagating direction, OB can be induced in NLCs for which $B_o > 0$ for **H**, **E** = 0. Consequently with the help of an additional magnetic field, OB

TABLE III

Summary of the predicted intrinsic optical bistability of the alkenyl room NLCs $m_3 = (1d_3CP,\ 0d_3CP)$ and $m_5 = (1d_3CAP,\ 0d_3CAP)$. The threshold intensities in W/cm^2 are calculated for a 250 μm thick-cell. The elastic constants are in $10^{-7} dyne$

NLC	k_{11}	k_{33}	n_o	n_e	B_o	Order	I_{th}	I'_{th}/I_{th}
m_3	12.29	36.5	1.493	1.646	−0.016	First	635	0.998
m_5	13.80	37.9	1.486	1.624	−0.001	First	738	0.999

has been observed in a nematic 4-n-pentyl-4'-cyanobiphenyl (5CB)[6] and can also be observed in all of the above five NLCs. As an example, we investigated the enhancement of OB in RO-TN-200. Let θ_m be the maximum deformation angle in the cell as defined in Refs. 2–5. Then θ_m is the deformation angle in the middle of the cell with respect to its initial orientation. The maximum deformation angle for RO-TN-200 as a function of light intensity and magnetic bias field strength at 22°C and wavelength 6328 Å is shown in Figure 1. Graph (a) in Figure 1 shows the dependence when using the old material parameters listed in Table I for RO-TN-200. Since $B_o < 0$, the transition was predicted[5] to be first order with $I'_{th} = 0.986 I_{th}$. For a cell of 250 μm thickness, the rising threshold intensity is $I_{th} = 209 W/cm^2$ and the falling threshold intensity is $I'_{th} = 0.986 I_{th} = 206 W/cm^2$. Graph (b) corresponds to the new material parameters listed in Table II for RO-TN-200. With the new parameters, $B_o > 0$ results and the predicted transition is second order without bistability for RO-TN-200.

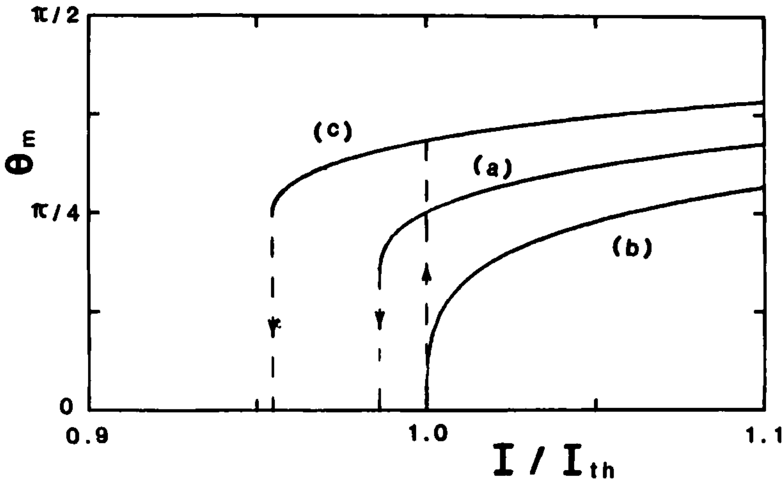

FIGURE 1 Maximum deformation angle as a function of reduced intensity I/I_{th} and magnetic field H/H_o for RO-TN-200 at temperature 22°C and wavelength 6328 Å In (a), the following old parameters are used: $k_{11} = 8.80 \times 10^{-7} dyne$, $k_{33} = 19.00 \times 10^{-7} dyne$, $n_o = 1.5345$, $n_e = 1.8100$. The predicted transition is first order with rising threshold intensity $I_{th} = 209 W/cm^2$ for a 250 μm thick-cell and the falling threshold intensity is $I'_{th} = 0.986 I_{th}$. In (b) and (c), the following new parameters are used: $k_{11} = 9.21 \times 10^{-7} dyne$, $k_{33} = 14.83 \times 10^{-7} dyne$, $n_o = 1.534$, $n_e = 1.795$. (b). $H = 0$. The predicted transition is second order with rising and falling threshold intensities both equal to $I_{th} = I_o = 170 W/cm^2$ for a 250 μm thick-cell. (c). $H = H_o$. The OB is enhanced and the transition becomes first order with rising threshold intensity $I_{th} = 3I_o = 510 W/cm^2$ for a 250 μm thick-cell. The falling threshold intensity is $I'_{th} = 0.954 I_{th} = 486 W/cm^2$.

The rising threshold intensity is $I_{th} = I_o = 170 W/cm^2$ for a 250 μm thick cell. Using the results presented in Ref. 5, we found that for a NLC with $B_o > 0$, OB can always be enhanced and the second-order transition will become a first-order transition in a bias magnetic field directed along the optical field propagating direction, provided the bias field strength is greater than the OB enhancement tricritical field $H^* = H_o\sqrt{16B_o/9u}$, where $H_o = (\pi/d)\sqrt{k_{33}/\chi_a}$ and χ_a is the magnetic susceptibility. The OB enhancement tricritical field is the critical field above which a second-order transition will become first-order. The enhancement of OB in RO-TN-200 by a bias magnetic field H is shown by graph (c) for $H = H_o > H^* = 0.15H_o$. The results show that OB is enhanced in RO-TN-200 with $I'_{th} = 0.954I_{th}$ by the bias field $H = H_o$. For d = 250 μm with $H = H_o$, $I_{th} = 3I_o = 510 W/cm^2$, $I'_{th} = 0.954I_{th} = 486 W/cm^2$, and the width of the OB cycle is $I_{th} - I'_{th} = 0.046I_{th} = 24 W/cm^2$. The rising threshold intensity is $I_{th} = 174\ W/cm^2$ at the tricritical field $H = H^* = 0.15H_o$. For a typical NLC, $\chi_a \sim 10^{-7}$ cgs unit, and $H_o \sim 300 - 600\ G$ for $d = 250 \mu m$. Thus using a low bias field ($< 500G$) directed along the optical field propagating direction, OB can be seen in RO-TN-200 at room temperature at low laser power ($I_{th} < 500 W/cm^2$).

In conclusion, new measurements are reported of the elastic constants and refractive indices of the room temperature nematics RO-TN-200, -201, -403 and E7. The new material parameters show that the purely optical field induced first-order Freedericksz transition can not be attained by these materials. However, the first order Freedericksz transition can be enhanced in these nematics by an external electric or magnetic bias field. We also found two room temperature nematic mixtures m_3 and m_5 for which the purely optical field induced first-order Freedericksz transition can be attained.

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