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In this paper we present a study of two similar, colorless molecular dopants designed to decrease the operating voltages of nematic liquid crystals by increasing the dielectric anisotropy. Experimental analysis shows that these materials reduced the threshold voltage (voltage associated with the Freedericksz transition) by up to 20%, but via a reduction in the liquid crystal order parameter. To gain insight into the decrease of the order parameter, we used density-functional and single-point MP2 theory to investigate the conformational preferences of our dopants; the calculations suggest that, because of steric interactions, the conformations adopted are rather rigid.

Keywords: colorless dopants; dielectric anisotropy; nematic liquid crystal; order parameter; steric hindrance; threshold voltage

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INTRODUCTION

The use of twisted nematic (TN) and super twisted nematic (STN) liquid crystal displays has become commonplace for portable electronic devices such as PDAs and cellular telephones. When designing displays for these portable (i.e., battery-powered) applications, careful attention must be placed on minimizing the required electrical power for the display drivers so as to increase battery lifetime. The design of these drivers must also take into account the threshold behavior of the response of nematic liquid crystalline materials in an applied electric field. This is the threshold voltage associated with the Freedericksz transition in nematic liquid crystals and is a function of the dielectric and elastic properties of the material. Resulting driver designs are then a compromise between minimizing power requirements and supplying the minimum required voltage levels to operate the display.

Although techniques exist to reduce the power requirements of liquid crystal displays for a given material and/or display geometry [1], one can also engineer the liquid crystal materials themselves such that their physical properties result in lower threshold voltages. By using this approach one could design new drive circuits with lower output voltages and in doing so reduce both the cost of the electronics and the power requirements.

Using the continuum theory of nematic liquid crystals developed first by Oseen [2] and later refined by Frank [3], Deuling [4] was able to show that the threshold voltage of homogeneously aligned nematic liquid crystalline materials is governed by the following relationship:

$$V_{th} = \pi\sqrt{\frac{k_{11}}{\Delta\varepsilon}} \tag{1}$$

Here, k_{11} is the splay elastic constant of the nematic material and $\Delta\varepsilon$ is the dielectric anisotropy at the driving frequency. From this relationship, the choices are either to decrease the splay elastic constant or to increase the dielectric anisotropy. A reduction in the elastic constant is unwise as the characteristic response time τ_0 scales inversely with the elastic constant:

$$\tau_0 = \frac{\gamma_1}{k_{11}}\left(\frac{d}{\pi}\right)^2 \tag{2}$$

In this equation γ_1 is the rotational viscosity coefficient of the material and d is the thickness of the liquid-crystal layer [5]. A significant increase in the response time will render the material unsuitable for display applications. An increase in the dielectric anisotropy is

therefore the preferred choice as its value has no direct impact on the switching dynamics or the optical properties of the material.

Implementing such an increase is nontrivial as the materials used for displays are mixtures of different liquid-crystalline materials (to ensure wide nematic range and to tune birefringence) where the resulting dielectric anisotropy is a linear combination of the values of the dielectric anisotropies of the different components. However, liquid-crystalline materials with large dielectric anisotropies tend to have large rotational viscosities [6], which would limit their maximum concentration (and hence usefulness) in commercial display mixtures.

An alternate approach explored in this work is to synthesize non-liquid-crystalline compounds that possess large dielectric anisotropies that can then be doped into existing liquid-crystalline materials to enhance the dielectric anisotropy and hence reduce the threshold voltage of the mixture. The goal is to synthesize materials where the dielectric anisotropy of the dopant is sufficiently large that it can be added at a fairly low loading level ($<10\%$) and enhance the dielectric anisotropy of the mixture without significantly reducing the mixture's order parameter. As the dopants do not need to be liquid crystalline, this presents an opportunity to investigate many more materials than would be possible if the materials were required to exhibit a liquid-crystalline phase.

The dielectric anisotropy of liquid crystals can be defined using the mean-field theory of Maier, Meier, and Saupe. Mean-field theory dictates that the dielectric anisotropy of a nematic liquid crystal is mainly a function of the magnitude of the dipole moment and the angle the dipole moment makes with the primary axis of the liquid crystal molecule.

$$\Delta\varepsilon = NhF\{\Delta\alpha - (F\mu^2/2kT)[1 - 3\cos^2(\beta)]\}S \tag{3}$$

Here N is the number density, h is the cavity field factor, F is the Onsager reaction field, $\Delta\alpha$ is the polarizability anisotropy, μ is the dipole moment, kT is the thermal energy, β is the angle between the dipole moment and the primary molecular axis, and S is the order parameter [7]. From Eq. (3) it can be inferred that if molecular dopants are to be synthesized to increase dielectric anisotropy, they should possess large dipole moments that make small angles with respect to the molecular axis and they should be compatible with the liquid-crystal host so as to not reduce the order parameter. Attempts at this approach in the literature utilized molecules in which a long alkyl group, to ensure compatibility with the liquid-crystal host, is attached to a polyene bridge, which at the other end is terminated with the large intrinsic dipole moment dicyanomethylidene group (Fig. 1a).

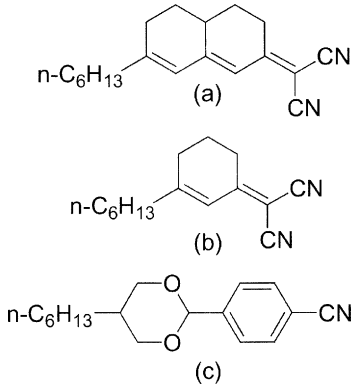


FIGURE 1 Chemical structures of (a) colored high-dielectric-anisotropy dopant, (b) colorless high-dielctric-anisotropy dopant, and (c) commercial PDX-3 colorless high-dielectric-anisotropy dopant.

Although successful in increasing $\Delta\varepsilon$, the high degree of conjugation led to absorption in the visible that was both undesirable for conventional TN/STN displays and without sufficient dichroic ratio to be used in guest–host-type displays [8]. Efforts to eliminate absorption in the visible (while still maintaining a large $\Delta\varepsilon$) by reducing the length of the polyene bridge (Fig. 1b) were successful but led to a decrease in the order parameter (and hence reduced nematic range and birefringence) for mixtures of the dopant and the commercial nematic mixture E7 available from Merck [9]. Colorless dopants with large dielectric anisotropies are available commercially from Merck (Fig. lc) and utilize two, large dipole moment moieties, dioxane, and a single cyano group. One such compound, labeled PDX-3, was added to the commercial nematic mixture E63 (Merck) and was successful in increasing the dielectric anisotropy of the mixture from the intrinsic value of 14.4 to 14.7 and 16.4 for addition of the dopant at the 3 and 5 wt% levels, respectively. This was accomplished without causing a significant reduction of the order parameter or increase in the rotational viscosity [9]. However, even at the 5 wt% doping level, the measured increase in the dielectric anisotropy results in a modest 5–6% decrease in the threshold voltage of the resulting mixture. Other compounds in this study possessed larger dielectric anisotropies but caused an undesirable increase in the rotational viscosity of the mixtures.

In this paper we investigate the use of a hybrid structure that incorporates the alkyl-dioxane-phenyl body of the commercial Merck dopant

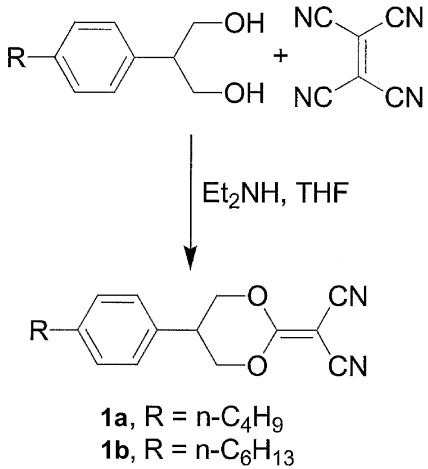
with the large dipole moment dicyanomethylidene group used by Wu et al. [8]. Large reductions (20%) of the threshold voltage were obtained with these materials. Our experimental and theoretical analysis strongly suggests that this reduction is caused by a reduction of the order parameter.

EXPERIMENTAL

Synthesis

For this study two new dopants (**1a** and **1b**) were synthesized according to Scheme 1.

Synthesis of 1a. Tetracyanoethylene (4.61 g, 36.0 mmol) was dissolved in 110 mL of tetrahydrofuran in a round-bottomed flask under argon. The diol [10] (5.768 g, 27.7 mmol) and diethyl amine (0.405 g, 5.54 mmol) were added to form a dark-colored reaction mixture, which was stirred at room temperature for 45 min. The solvent was then removed under reduced pressure and the crude product was recrystallized from benzene / hexanes (1:1) to give **1a** as colorless crystals 1.14 g (4.2 mmol 15%). ^{1}H Nuclear Magnetic Resonance, (NMR) (500 MHz, $CDCl_3$) δ 7.12 (d, $J = 8$ Hz, 2H), 6.99 (d, $J = 8$ Hz, 2H), 4.62 (dd, $J = 11$ Hz, 5 Hz, 2H), 4.42 (apparent t, $J = 11$ Hz, 2H), 3.46 (tt, $J = 11$, 5 Hz, 1H), 2.49 (t, $J = 7$ Hz, 2H), 1.46 (apparent quint., $J = 7$ Hz, 2H), 1.22 (apparent sext., $J = 7$ Hz, 2H), 0.75 (t, $J = 7$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$ δ 174.0, 144.1, 129.5, 127.3, 112.878, 71.8, 37.1, 35.1, 33.3, 22.1, 13.7. EIMS m/z 282 (M^+). Anal. calcd. For $C_{17}H_{18}N_2O_2$: C,



SCHEME 1

72.32; H; 6.43; N, 9.92; O, 11.33. Found: C, 72.11; H, 6.41; N, 9.95. UV-vis (MeCN) $\lambda_{max}(\varepsilon_{max})$ 254 (26 000) nm ($M^{-1}cm^{-1}$). DSC: mp = 102°C; $\Delta H_{fus} = 3.8$ kcal mol^{-1}.

Synthesis of 1b. Dopant 1b was obtained as white crystals (0.45 g, 1.37 mmol, 38%) from tetracyanoethylene (0.600 g, 4.68 mmol) and the appropriate diol [10] (0.850 g, 3.60 mmol) after synthesis and purification analogous to that of **1a**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, $J = 9$ Hz, 2H), 7.09 (d, $J = 9$ Hz, 2H), 4.73 (dd, $J = 11$ Hz, 5 Hz, 2H), 4.54 (t, $J = 11$ Hz, 2), 3.53 (tt, $J = 11, 5$ Hz, 1H), 2.59 (t, $J = 8$ Hz, 2), 1.53–1.62 (m, 2H), 1.25–1.34 (m, 6H), 0.86 (t, $J = 8$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 144.4, 129.7, 129.5, 127.3, 112.7, 71.8, 45.4, 37.3, 35.5, 31.6, 31.2, 28.5, 22.5, 14.0. EIMS m/z 310 (M^+). Anal. calc. For $C_{19}H_{22}N_2O_2$: C, 73.52; H, 7.14; N, 9.09; O, 10.31. Found: C, 73.68; H, 7.33; N, 9.10. UV-vis(MeCN) $\lambda_{max}(\varepsilon_{max})$ 252 (24 000) nm ($M^{-1}cm^{-1}$). DSC: mp = 110°C; $\Delta H_{fus} = 6.9$ kcal mol^{-1}.

Sample Preparation

To study the effect of these materials on liquid crystals, they were dissolved in the commercial nematic mixture E7 (Merck) heated above the clearing temperature ($T_C = 61$°C) and then allowed to cool to room temperature (26°C). Solutions were made for each compound at the 2, 5, and 10 wt% loading level. Sample cells to study the properties of the mixtures were constructed from Indium Tin Oxide-coated glass substrates with poly (vinyl alcohol) films spun from aqueous solution as the alignment layer. The alignment layers were buffed with a velvet cloth in antiparallel directions to produce homogeneous alignment. The cell thickness was set at 5 micrometers by glass spacers (Merck) and checked by the interference method [5]. The sample cells were constructed empty, heated above the clearing temperature to 70°C, and then filled with the liquid-crystal mixtures by capillary action. The filled cells were held at 70°C for 1 h and then allowed to cool to room temperatrue at 0.5°C/min, where all further measurements were made.

RESULTS AND DISCUSSION

Synthesis

The new dopants **1a** and **1b** were synthesized by the base-catalyzed reaction of the appropriate diols (both prepared by a literature procedures [10]) with tetracyanoethylene (see Scheme 1) [11]; both are colorless crystalline solids. The different alkyl end groups serve to tune the solubility of the dopants in the LC host.

Material Analysis

Differential scanning calorimetry (DSC) was used to measure the melting points and heat-fusion enthalpies of the two compounds. Maintaining low values of the melting point and heat of fusion are important as the goal is to form a eutectic mixture of the dopant with the liquid crystal [8]. Compound **1a** had a heat of fusion of 3.79 kcal/mol and a melting point of 102°C whereas compound **1b** had a heat of fusion of 6.94 kcal/mol and a melting point of 110°C. These values of the heat of fusion are comparable with the previously utilized materials (7.51 kcal/mol and 5.32 kcal/mol for structures in Figs. 1a and 1b, respectively). The melting points of our materials are comparable with that of the compound in Fig. 1a (62.3°C) whereas the compound shown in Fig. 1b is a liquid at room temperature (melting point is 5.93°C). The linear absorption spectrum of compound **1a** (Fig. 2) shows that it is transparent throughout the visible region of the spectrum. The absorption of compound **1b** is nearly identical to that of **1a**. These measurements indicate that the two compounds should be compatible with a nematic liquid-crystal host and suitable for display applications.

Electro-Optic Analysis

Using the voltage-dependent phase-change method [5], retardation data as a function of applied voltage was collected at 633 nm

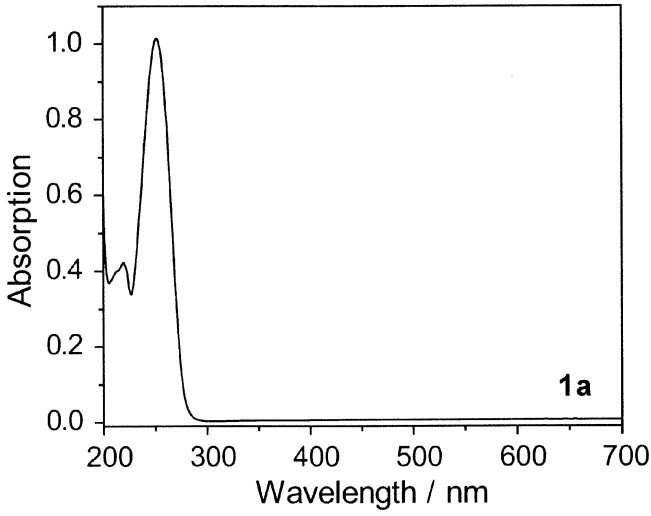


FIGURE 2 Linear absorption spectrum of compound **1a**.

(Figs. 3a, 3b) for each of the cells. A 1.0 kHz sinusoidal signal was used as the driving voltage. Threshold voltages were determined by extrapolating the data back to zero retardation within the linear region just above threshold. At the 2 wt% doping level the reduction in the threshold voltage has already exceeded the 6.4% reduction by the PDX-3 compound at the 5 wt% loading level (a 9.7% reduction for the **1a** mixture and a 7.4% reduction for the **1b** mixture). The maximum measured reductions in the threshold voltage, measured at the 10 wt% loading level, were 21.0% for the **1a** material and 20.1% for the **1b** material. This reduction can be due to either an increase in dielectric anisotropy or a decrease in the splay elastic constant, as shown in Eq. (1). To investigate its origin, the dielectric anisotropy was measured with an LCR meter using the single-cell method [5]. These values, along with the measured threshold voltages, were then used to calculate the splay elastic constant. Values for the dielectric anisotropy and splay elastic constant are shown as a function of dopant concentration in Fig. 4a and the data show that both the dielectric anisotropy and the splay elastic constant decrease with concentration. Figure 4b shows the same data on a percent reduction scale and indicates that the splay constant decreases faster with concentration than the dielectric anisotropy. A possible explanation for this can be found from mean-field theory.

Maier and Meier [7] show with Eq. (3) that the dielectric anisotropy is linear with the order parameter, but in addition to this, Saupe [12] shows that the elastic constants of a nematic liquid crystal are quadratic with order parameter:

$$k_{ii} = C_{ii} V_n^{-7/3} S^2 \tag{4}$$

Here, the k_{ii} are the elastic constants, C_{ii} are the reduced elastic constants, V_n is the mole volume, and S is the order parameter. Thus, as the elastic constants decrease faster with order parameter than the dielectric anisotropy, we hypothesize that the dopants are decreasing the order parameter and hence the threshold voltage of the liquid-crystal mixture.

To further investigate this possible reduction in order parameter, voltage-dependent phase-change data (to determine birefringence) and clearing temperatures (T_c) measured by DSC for the different mixtures were used to plot birefringence as a function of reduced temperature at an ambient temperature (T) of 26°C (Fig. 5). Haller [13] has shown that over the entire nematic range the birefringence (Δn) can be expressed as

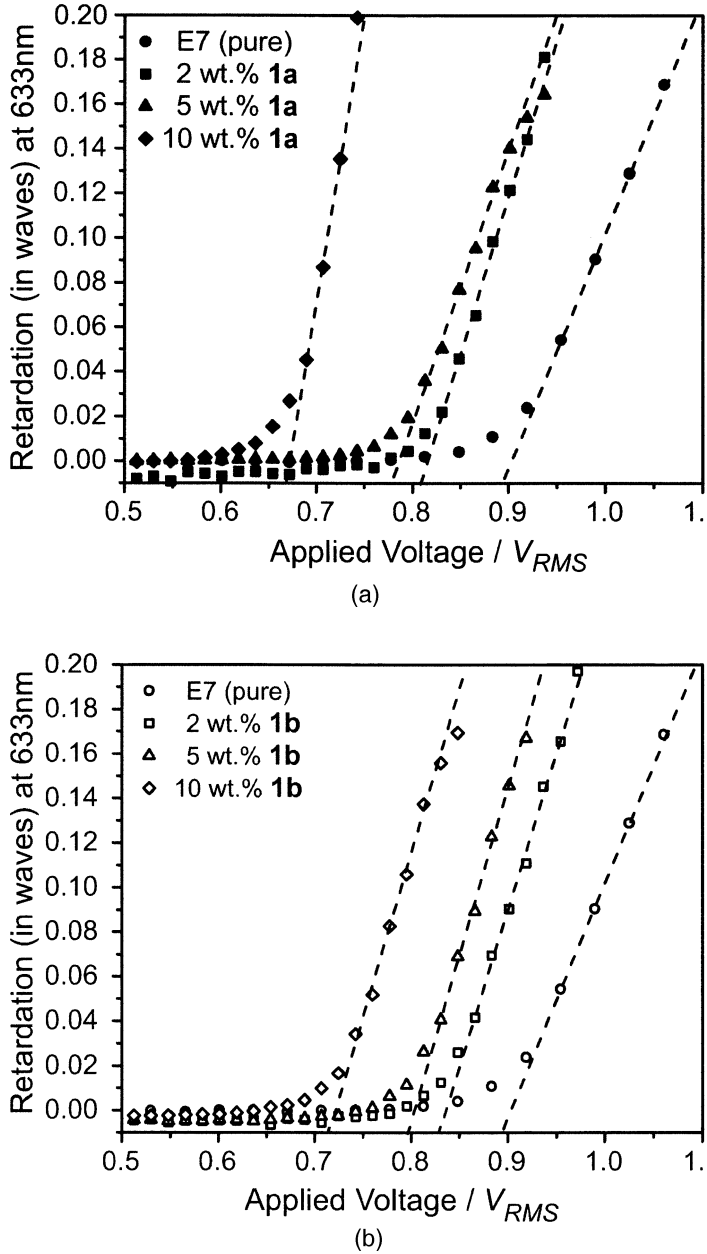


FIGURE 3 (a) Retardation data and extrapolated threshold voltages as a function of applied voltage for mixtures containing increasing amounts of compound **1a** and (b) retardation data and extrapolated threshold voltages as a function of applied voltage for mixtures containing increasing amounts of compound **1b**.

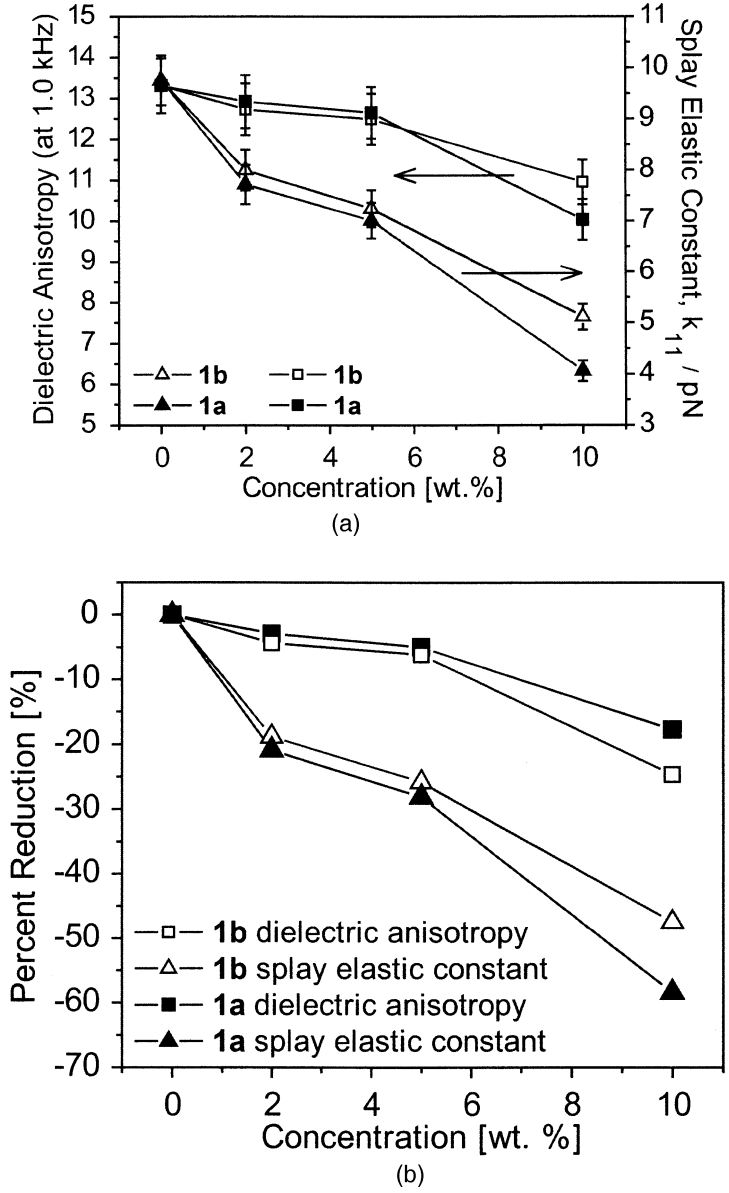


FIGURE 4 (a) Dielectric anisotropy and splay elastic constant as a function of dopant concentration for mixtures containing increasing amounts of compounds **1a** and **1b** and (b) reduction of dielectric anisotropy and splay elastic constant plotted as a function of dopant concentration for mixtures containing increasing amounts of compound **1a** and **1b**.

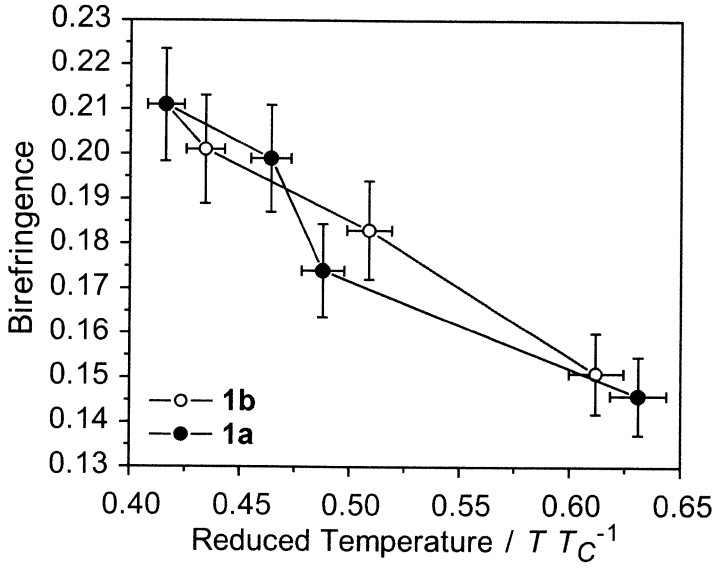


FIGURE 5 Birefringence (measured at 633 nm) as a function of reduced temperature for mixtures containing the **1a** and **1b** compounds.

$$\Delta n = \Delta n_0 (1 - T/T_C)^{\beta} = \Delta n_0 S \tag{5}$$

Here Δn_0 is the birefringence defined for $S = 1$, the ratio T/T_C is the reduced temperature (ratio of ambient temperature to the clearing temperature), and β is a constant. Using this relationship we can fit the data in Fig. 5 to Eq. (5) to calculate the value of S directly. In addition, from Eq. (4), a plot of the splay elastic constant against the square of the order parameter should fit a straight line through the origin. This is indeed the case, as can be seen from Figs. 6a and 6b. We conclude from these experimental results that even though the dopants were successful in reducing the threshold voltage, they did so by a reduction in order parameter and not an increase in the dielectric anisotropy.

Theoretical Analysis

Although we have shown experimentally that a reduction in the order parameter is the reason for the reduced threshold voltages, we have used quantum-chemical methods to provide a tentative explanation for the cause of the reduction. For comparison, analysis was also carried out on the Merck PDX-3 structure (Fig. 1c) [9]. This material has

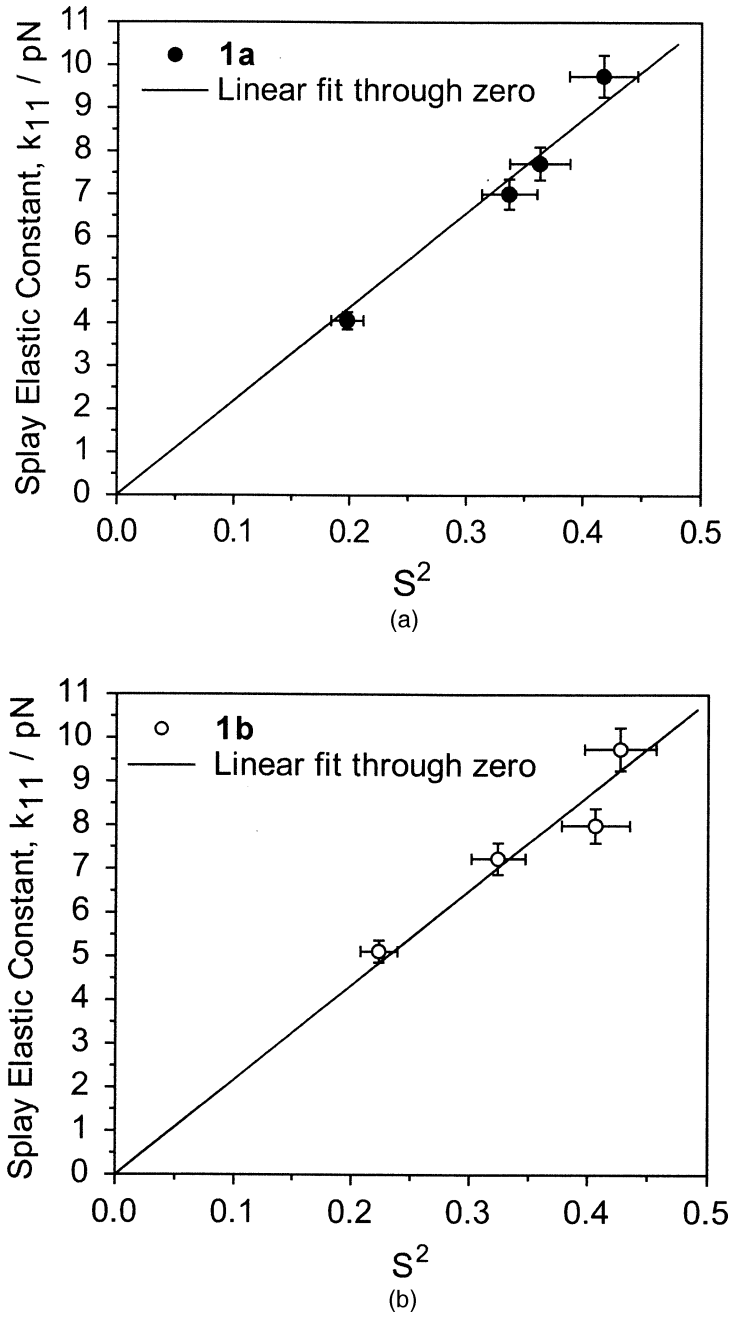


FIGURE 6 (a) Splay elastic constant data and linear fit as a function of the square of the order parameter for mixtures containing compound **1a** and (b) splay elastic constant data and linear fit as a function of the square of the order parameter for mixtures containing compound **1b**.

similarities in structure with our materials but has been reported to increase the dielectric anisotropy of nematic liquid-crystal mixtures.

Possible conformers have been considered to find the most stable geometry for each of the compounds. Molecular geometries have been optimized for the different structures at the density-functional theory level using the B3LYP exchange-correlation functional and a 6-31G** basis set [14–16]. In addition, vibrational frequency calculations were performed to characterize the nature of the stationary points. In all cases the terminal alkyl chain was modeled by a methyl group. Subsequent to this, torsional potential-energy surfaces were investigated for the most stable conformer in each case to try to gain insight into the behavior of the material when mixed into a liquid-crystal host. The relative energy was calculated for torsion angles, ϕ, between 0° and 180° in 10° increments with all other geometric parameters optimized for each angle. We define ϕ in Figs. 7a and 7b as the angle formed between the planes defined by $\angle H_1C_2C_3$ and $\angle C_2C_3C_4$ with $\phi = 0°$ roughly corresponding to the dioxane and phenyl rings being perpendicular to each other.

The most stable conformers for the **1a/1b** and PDX-3 structures are shown in Figs. 8a and 8b, respectively. In each case the most

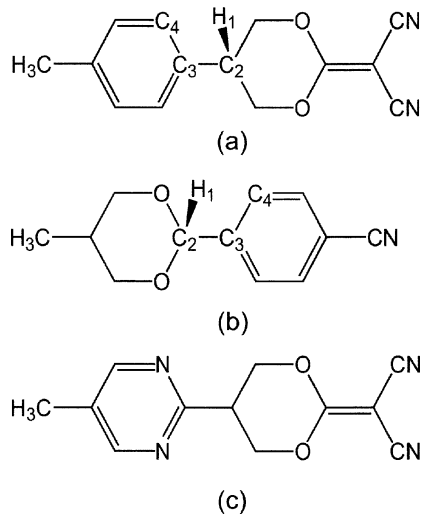


FIGURE 7 Schematic diagram of (a) **1a/1b** and (b) PDX-3 compounds illustrating how the torsional angle ϕ is defined as the phenyl and dioxane rings rotate about the C_2-C_3 carbon single bond. Structure (c) is the proposed compound **2**.

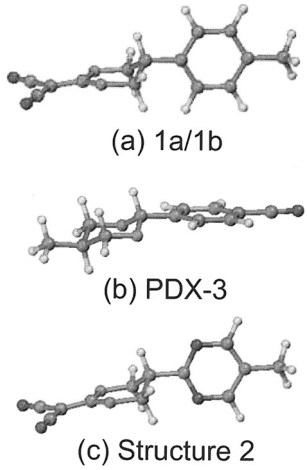


FIGURE 8 Optimized geometries obtained from density-functional theory calculations.

stable geometry is a linear one (similar to liquid-crystal molecules) with the aromatic and dioxane structures being orthogonal ($\phi = 0^\circ$) for **1a**/**1b** and copolanar ($\phi = 90^\circ$) for PDX-3. By looking at the relative energies as a function of torsional angle (Fig. 9), we see that the energy required to twist the **1a**/**1b** molecule from $\phi = 0^\circ$ to $\phi = 90^\circ$ is 2.8 kcal/mol, three times the 0.9 kcal/mol required to have the PDX-3 molecule go from $\phi = 90^\circ$ to $\phi = 0^\circ$. Refinement of the estimation of the rotational energy barrier using single-point MP2/6-31G** calculations [17] yielded an energy barrier of 3.1 kcal/mol for the **1a**/**1b** molecule and 0.8 kcal/mol for the PDX-3 molecule; thus, the higher-level MP2 theory provides a ratio of nearly 4 for the rotational barriers. Presumably the high energy of the planar conformation is due to steric interactions between hydrogen atoms on the phenyl ring and dioxane ring in the positions next to the ring junction; in PDX-3 these interactions are reduced because here the relevant positions in the dioxane ring are occupied by oxygen atoms, rather than by CH_2 groups. Hence, we hypothesize that the stiffness of the **1a**/**1b** structures (and resulting inability to conform to the local liquid crystalline environment) can disturb the liquid-crystalline phase of their host and explains the observed reduction in the order parameter.

Based on these findings, we propose a new liquid-crystal dopant (structure **2**) based on our **1a**/**1b** structure, as shown in Fig. 7c. In this new structure we have achieved a reduction of steric hindrance by the

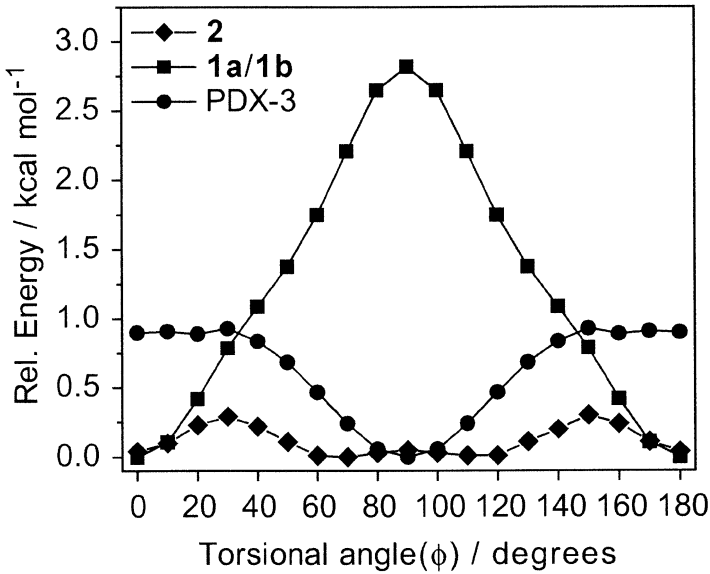


FIGURE 9 Relative energies for different isomers of the three structures shown in Fig. 7 as a function of the torsional angle ϕ.

substitution of nitrogen atoms into the phenylene ring. This structure was evaluated in the same manner as the others using density-functional theory and MP2 calculations, and the results are promising. The most stable conformer is again linear, suggesting good compatibility with a liquid-crystal host (Fig. 8c) and the torsional analysis shows that the energy required for twisting is much less than either of the other two compounds (Fig. 9), with barriers on the order of kT at room temperature.

CONCLUSION

We have studied two colorless, molecular dopants for the reduction of the threshold voltage in nematic liquid crystals by an increase in the dielectric anisotropy of the resulting mixture. Experimental analysis has shown that although these materials were successful in reducing the threshold voltage by 20%, they did so by a decrease in the liquid-crystal order parameter. Based on density-functional theory and MP2 calculations, we hypothesize that the reduction in order parameter can be attributed to the steric hindrance of the rigid dopants. Finally, a new structure based on our results is proposed.

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