Chem. Mater. **2002,** *14,* 773−776

Electro-Optic Switching by Helicene Liquid Crystals

Colin Nuckolls,[†] Renfan Shao,[‡,||] Won-Gun Jang,[‡,||] Noel A. Clark,[‡,||]
David M. Walba,[§,||] and Thomas J. Katz*[,†]

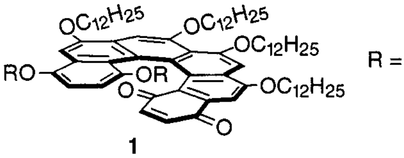
Department of Chemistry, Columbia University, New York, New York 10027, Department of Physics, University of Colorado, Boulder, Colorado 80309, Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309, and Ferroelectric Liquid Crystal Materials Research Center, University of Colorado, Boulder, Colorado 80309

Received July 24, 2001. Revised Manuscript Received November 12, 2001

Binary mixtures of the aggregating helicene **1** with dodecane have, at dodecane concentrations $>$30 vol %, a nematic liquid crystalline phase and, at dodecane concentrations $\lesssim$5 vol %, a hexagonal columnar liquid crystalline phase. The helical structure with donor and acceptor groups at opposite ends gives rise to a molecular dipole moment that is parallel to the helix axis and a positive dielectric anisotropy. Accordingly, the helix axes orient parallel to an applied electric field, providing the basis for electro-optic switching.

Introduction

The ability to orient molecular dipoles is an important element in the design of useful liquid crystalline materials. Cyanobiphenyls (CBs) are the best known.[1] In these, the dipole moments of the cyano groups endow the nematic and smectic phases with dielectric anisotropies, $\Delta\epsilon$, that are large and positive (that is, with dielectric constants that are larger parallel to the molecules' long axes than perpendicular to them) and threshold switching voltages that are small.[2] Similar properties would be expected for disk-shaped molecules that have large dipole moments *normal* to the molecular plane, but only few such structures are known.[3−6] In this paper, we show that enantiopure helicene **1**,[7] which has a molecular dipole moment approximately parallel to the helix axis, does have such properties and can be used for electro-optic switching.



1

For molecules that are rod shaped, electrostatic energy is minimized when the dipole moments of neighboring rods are oriented antiparallel.[8] Accordingly, $\epsilon_{\|}$ for 4′-pentyl-4-cyanobiphenyl, while large,[9] is less than it would be[10] were it not reduced by the correlation of the molecules' dipole moments.[11] In contrast, for columnar discotic materials that have dipole moments perpendicular to the disks, electrostatic energy is minimized when the moments of stacked molecules are arranged parallel, head-to-tail.[8a] Solutions of disk-shaped molecules therefore have polarizabilities that are particularly large.[12] In addition, in enantiopure helicene **1**, head-to-tail orientation should be favored by steric effects that keep the bulkier ends of the molecules apart. Moreover, because the dipole moment is derived from displacement of charge along the core, it should be larger in molecules such as **1** than in discotic molecules in which the moment is derived from the alignment of polar side chains.[13−15] Accordingly, the dielectric anisotropy of columns of **1** is expected to be both positive and large.

The experiments described below measure how electric fields affect the depolarization of light that has passed through transparent capacitor electro-optic cells containing enantiopure **1** and thereby probe how electric

---

[*] To whom correspondence should be addressed. Tel: (212)854-2173. Fax: (212)932-1289. E-mail: TJK1@Columbia.edu.

[†] Columbia University.

[‡] Department of Physics, University of Colorado.

[§] Department of Chemistry and Biochemistry, University of Colorado.

[||] Ferroelectric Liquid Crystal Materials Research Center, University of Colorado.

(1) Gray, G. W.; Harrison, K. J.; Nash, J. A. *Electron. Lett.* **1973**, *9*, 130.

(2) $\Delta\epsilon = \epsilon_{\|} - \epsilon_{\perp}$, where $\epsilon_{\|}$ and $\epsilon_{\perp}$ are the dielectric constants when the electric field is parallel and perpendicular, respectively, to the long molecular axis.

(3) Piechocki, C.; Boulou, J.-C.; Simon, J. *Mol. Cryst. Liq. Cryst.* **1987**, *149*, 115.

(4) (a) Kilian, D.; Knawby, D.; Athanassopoulou, M. A.; Trzaska, S. T.; Swager, T. M.; Wrobel, S.; Haase, W. *Liq. Cryst.* **2000**, *27*, 509. (b) Zheng, H.; Carroll, P. J.; Swager, T. M. *Liq. Cryst.* **1993**, *14*, 1421. (c) Zheng, H. X.; Lai, C. K.; Swager, T. M. *Chem. Mater.* **1995**, *7*, 2067. (d) Serrette, A. G.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 8879. (e) Serrette, A. G.; Swager, T. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2342. (f) Xu, B.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 1159.

(5) (a) Zimmermann, H.; Poupko, R.; Luz, Z.; Billard, J. *Z. Naturforsch., A: Phys. Sci.* **1985**, *40a*, 149. (b) Malthête, J.; Collet, A. *J. Am. Chem. Soc.* **1987**, *109*, 7544. (c) Levelut, A. M.; Malthête, J.; Collet, A. *J. Phys.* **1986**, *47*, 351. (d) Wang, L.; Sun, Z.; Pei, X.; Zhu, Y. *Chem. Phys.* **1990**, *142*, 335. (e) Jákli, A.; Saupe, A.; Scherowsky, G.; Chen, X. H. *Liq. Cryst.* **1997**, *22*, 309.

(6) Cometti, G.; Dalcanale, E.; CuVosel, A.; Levelut, A. M. *J. Chem. Soc., Chem. Commun.* **1990**, 163.

(7) Nuckolls, C.; Katz, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 9541.

(8) Dunmur, D. A.; Palffy-Muhoray, P. *Mol. Phys.* **1992**, *76*, 1015.

(9) (a) Dunmur, D. A.; Manterfield, M. R.; Miller, W. H.; Dunleavy, K. *Mol. Cryst. Liq. Cryst.* **1978**, *45*, 127. (b) Bogi, A.; Faetti, S. *Liq. Cryst.* **2001**, *28*, 729 and references therein.

(10) Raszewski, Z.; Rutkowska, J.; Kedzierski, J.; Zeilinski, J.; Perkowski, P.; Piecek, W.; Zmija, J. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1994**, *251*, 357.

(11) Toriyama, K.; Dunmur, D. A. *Mol. Phys.* **1985**, *56*, 479.

(12) Dalton, L. R.; Harper, A. W.; Robinson, B. H. *Proc. Natl. Acad. Sci.* U.S.A. **1997**, *94*, 4842.

10.1021/cm010628o CCC: $22.00

fields affect the orientation of the molecules. The stacks reorient to be parallel to an applied electric field (as long as it exceeds a threshold value), implying that their dielectric anisotropy is positive. The speed of the reorientation depends on the temperature of the sample, on the amount of diluent, and on the strength of the voltage applied.

Results and Discussion

The helicene was first examined as the neat material. Enantiopure **1** in a rubbed 4 μm cell was heated to ca. 100 °C, at which temperature it is isotropic, and then cooled into its columnar phase.[7] A photomicrograph of the texture at 80 °C is shown as Figure 1a. The material's birefringence means that all components of the optic axis cannot be perpendicular to the cell surface, and its disordered Schleiren-like texture shows that the rubbed cell surfaces do not orient the in-plane structure. Application of at least 60 V causes the sample to become optically isotropic. The implications are that the material is uniaxial and that its optic axis reorients to the plates' normal. The planar alignment can be recovered by heating the sample until it is isotropic and then cooling it, but it cannot be recovered with any practical speed by altering the electric field. This experiment shows that the columns orient parallel to electric fields above a threshold value, but like other columnar materials,[4a,16] the material's high viscosity prevents the columns from realigning parallel to the surface when the electric field is removed.

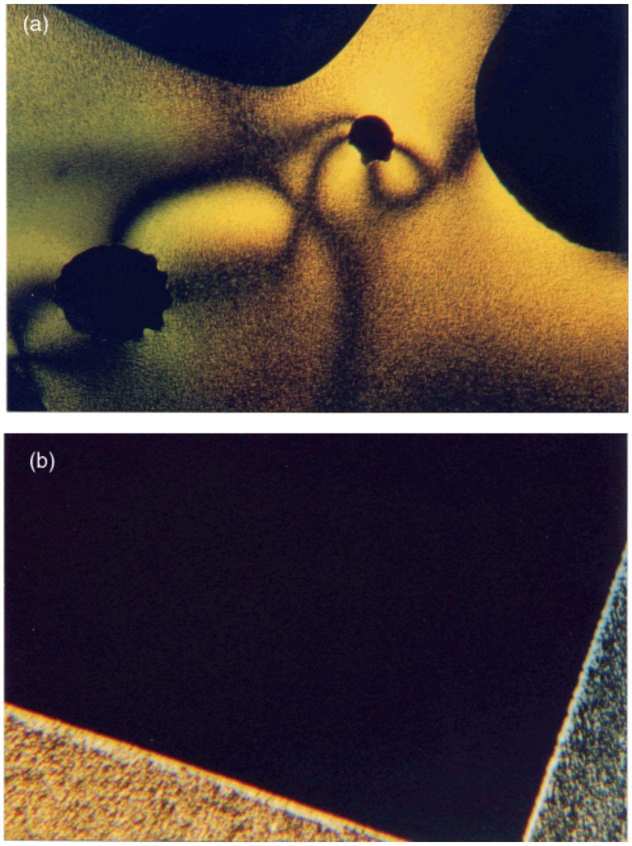


Figure 1. (a) Microscopic view of pure (+)-**1** that had been cooled from the clearing temperature to 80 °C in a 4 μm nylon-lined cell. The sample is between crossed polarizers. (b) Microscopic view of a 17 wt % solution of (+)-**1** in dodecane in a 4 μm nylon-lined cell in an electric field of 3.1 V μm^{-1}. The sample is between crossed polarizers. The area covered by the electrodes (which are transparent) is black because the helix axes have been aligned normal to the plates; the other areas are aligned with the helix axes parallel to the plates and are therefore bright.

The viscosity was therefore reduced by diluting the samples with dodecane, and the experiments were repeated.[17−19] The reason for choosing this approach is that when its concentration in dodecane is as low as 3 wt %, **1** has previously been shown to aggregate into columns.[7,20] To test the effects of dilution, a 17 wt % solution of **1** in dodecane was heated in a cell until the sample was isotropic. When it was then cooled to 50 °C, it became birefringent, with the optic axis, as before, parallel to the plates but this time partially ordered by the rubbing. Between crossed polarizers, light was transmitted fairly uniformly across the cell's surface if (and only if) the rubbing direction differed from the directions of the polarizer and analyzer axes. As in the case of the neat material, the light was totally extinguished (Figure 1b) when an electric field was applied. In this figure, the material covers the entire area, but extinction occurs only where the electrodes overlap. When the electric field was turned off, the transmission of light was restored. The implications are that the solution has an optic axis that, in the absence of an electric field, is parallel to the plates and, when an

---

(13) (a) Bock, H.; Helfrich, W. *Liq. Cryst.* **1992**, *12*, 697. (b) Bock, H.; Helfrich, W. *Liq. Cryst.* **1995**, *18*, 387. (c) Scherowsky, G.; Chen, X. H. *J. Mater. Chem.* **1995**, *5*, 417. (d) Jákli, A. Müller, M.; Krüerke, D.; Heppke, G. *Liq. Cryst.* **1998**, *24*, 467. (e) Barberá, J.; Iglesias, R.; Serrano, J. L.; Sierra, T.; de la Fuente, M. R.; Palacios, B.; Pérez-Jubindo, M. A.; Vázquez, J. T. *J. Am. Chem. Soc.* **1998**, *120*, 2908. (f) Serrano, J. L.; Sierra, T. *Chem.—Eur. J.* **2000**, *6*, 759. (g) Heppke, G.; Krüerke, D.; Löhning, C.; Lötzsch, D.; Moro, D.; Müller, M.; Sawade, H. *J. Mater. Chem.* **2000**, *10*, 2657.

(14) The dielectric constant is smaller when parallel than when perpendicular to the short axis of discogens as long as the side chains are not attached by ester linkages. (a) Heppke, G.; Ranft, A.; Sabaschus, B. *Mol. Cryst. Liq. Cryst., Lett. Sect.* **1991**, *8*, 17. (b) Raghunathan, V. A.; Madhusudana, N. V.; Chandrasekhar, S.; Destrade, C. *Mol. Cryst. Liq. Cryst.* **1987**, *148*, 77.

(15) (a) Palmans, A. R. A.; Vekemans, J. A. J. M.; Hikmet, R. A.; Fischer, H.; Meijer, E. W. *Adv. Mater.* **1998**, *10*, 873. (b) Usol'tseva, N.; Hauck, G.; Koswig, H. D.; Praefcke, K.; Heinrich, B. *Liq. Cryst.* **1996**, *20*, 731. (c) Krüerke, D.; Rudquist, P.; Lagerwall, S. T.; Sawade, H.; Heppke, G. *Ferroelectrics* **2000**, *243*, 207.

(16) Reported switching times are as follows: 1 s at 90 °C and 8 V μm^{-1} in ref 13a; 0.1 ms to 100 s in ref 13b; 15−50 ms in ref 13c; several seconds at 100 °C in ref 13e.

(17) Palmans et al., ref 15a, used dodecane as a solvent and Usol'tseva et al., ref 15b, used pentadecane. Both achieved switching by using disk-shaped mesogens, but the switching times were long: hours for Usol'tseva et al.; between 5 and 350 s for Palmans et al. depending on the field strength (4.1−10 V μm^{-1}) and temperature (20−80 °C). Krüerke et al., ref 15c, extended the procedure reported here, and their results are comparable to ours.

(18) Other examples of disk-shaped mesogens organizing into columns in organic solvents: (a) Sheu, E. Y.; Liang, K. S.; Chiang, L. Y. *J. Phys. (Paris)* **1989**, *50*, 1279. (b) Gabriel, J.-C.; Larsen, N. B.; Larsen, M.; Harrit, N.; Pedersen, J. S.; Schaumburg, K.; Bechgaard, K. *Langmuir* **1996**, *12*, 1690. (c) Schutte, W. J.; Sluyters-Rehbach, M.; Sluyters, J. H. *J. Phys. Chem.* **1993**, *97*, 6069. (d) Usoltseva, N.; Praefcke, K.; Blunk, D.; Smirnova, A. *Bull. Russ. Acad. Sci., Phys. Ser.* **1998**, *62*, 1325.

(19) Other helical aromatic molecules that assemble into columns in organic solvents: (a) Nuckolls, C.; Katz, T. J.; Katz, G.; Collings, P. J.; Castellanos, L. *J. Am. Chem. Soc.* **1999**, *121*, 79. (b) Nuckolls, C.; Katz, T. J.; Verbiest, T.; Van Elshocht, S.; Kuball, H.-G.; Kiesewalter, S.; Lovinger, A. J.; Persoons, A. *J. Am. Chem. Soc.* **1998**, *120*, 8656. (c) Lovinger, A. J.; Nuckolls, C.; Katz, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 264. (d) Fox, J. M.; Katz, T. J.; Van Elshocht, S.; Verbiest, T.; Kauranen, M.; Persoons, A.; Thongpanchang, T.; Krauss, T.; Brus, L. *J. Am. Chem. Soc.* **1999**, *121*, 3453.

(20) These are similar to other helical aromatic molecules that assemble into columns in organic solvents: see ref 19.

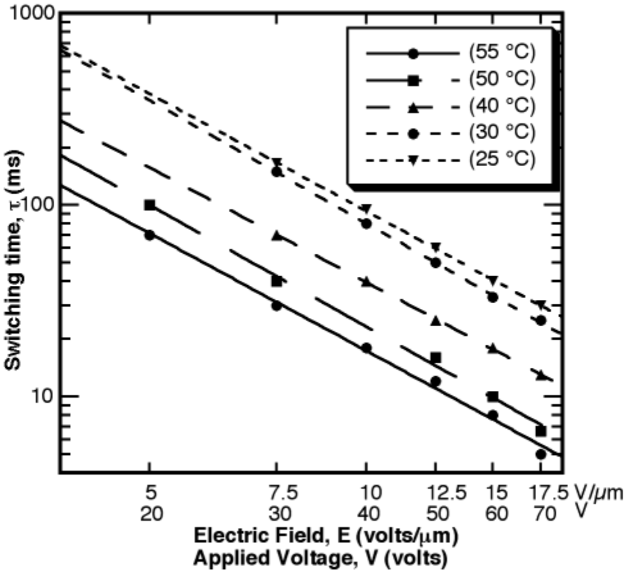


Figure 2. Log−log plot for a series of temperatures of electro-optic switching times $\tau(E)$ against the electric field strength for the field-induced planar-homeotropic reorientation of helicene **1** as a 17 wt % solution in dodecane. The best least-squares lines are drawn through the experimental points.

electric field is applied, reorients normal to the plates.

The electro-optic response for a change in transmission from 10 to 90% was measured as a function of applied electric field, which was stepped from zero to E at time zero and then alternated between $+E$ and $-E$ at 1 Hz. The measurements were made at five temperatures, and the data are plotted in Figure 2. Although they are not as fast as for some columnar ferroelectric materials,[4a] the switching times for **1** are relatively fast for a discotic liquid crystal:[15,16] at 55 °C, they are 18 ms when $E = 10$ V μm^{-1} and 5 ms when $E = 17.5$ V μm^{-1}. The data fit the function $\tau = aE^{-x} + b$ (Figure 2) with $x = 2.06 \pm 0.05$ and $b \approx 0$, implying that $\tau(E,T) \cong a(T)E^{-2}$. The inverse square dependence of the switching time on electric field is characteristic of reorientations of liquid crystal directors that are driven by dielectric torques,[21] with one power of E inducing a dipole and the other the torque on it. The implication is that the nematic phase of **1** lacks long-range polar order.[22] Moreover, the absence of hysteresis and threshold and the broad range of E over which the inverse square dependence prevails are characteristic of nematic phases. For these, $\tau(E,T) \cong [\gamma(T)/\Delta\epsilon(\mathrm{T})]E^{-2}$, where T is the absolute temperature, $\gamma(T)$ is the orientational viscosity, and $\Delta\epsilon(T)$ is the dielectric anisotropy. Accordingly, the strong dependence of $\tau(E,T)$ on temperature is attributed to the viscosity varying with temperature. The Arrhenius activation energy, 11.90 ± 0.7 kcal/mol, is typical of thermotropic discotic nematics.[23]

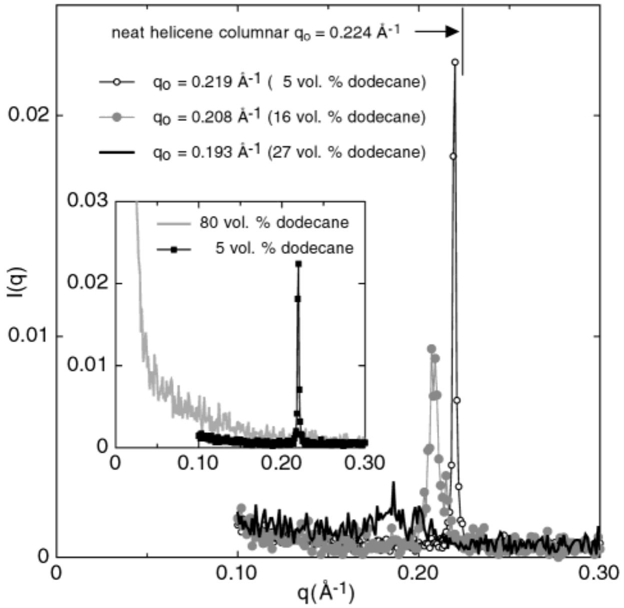


Figure 3. Diffracted X-ray intensity vs wave vector q for helicene−dodecane mixtures at 64 °C. The inset compares diffraction at the highest and lowest dodecane concentrations.

X-ray diffraction was used to analyze the structures of the helicene−dodecane mixtures. Unoriented samples were studied at 64 °C as the dodecane concentration was changed. The results are shown in Figure 3. The neat helicene columnar phase exhibits a sharp Bragg reflection peak at a wave vector $q_o = 0.224$ Å^{-1} ($d = 28.0$ Å), the (01) reciprocal lattice vector of the hexagonally ordered columns. At the dodecane concentrations used for the electro-optic measurements (80 vol % dodecane), no Bragg reflection is seen. The mixture is nematic. However, when the dodecane concentration is decreased to ca. 30 vol %, a broadened diffraction peak appears, indicative of pretransitional fluctuations to short-range columnar order as the nematic material approaches the columnar phase. At this concentration, the correlation length for columnar ordering is about 300 Å. As the dodecane concentration is lowered further, this peak narrows in width and grows in intensity approaching that of the neat helicene at about 5 vol % dodecane. The peak also shifts in position, a result of dodecane swelling the column lattice.

Conclusions

The electro-optic effect shows that the phase obtained in the helicene−dodecane mixtures is a discotic nematic with positive dielectric anisotropy. The electric field dependence of the electro-optic response shows that the nematic is nonpolar, i.e., that the projections of the longitudinal molecular dipoles along the mean disk normal vary randomly in sign. The switching times, which depend on the ratio of dielectric to viscous torques, are fast when compared to those of other discotic nematics, suggesting that the dielectric anisotropy is relatively large.

Experimental Section

The electro-optic effects were studied by means of polarized transmitted light microscopy, using samples of the material contained in transparent capacitors made of glass plates that were coated with indium−tin oxide (ITO) and spaced by 4 μm. The ITO electrodes were coated with a 200 Å thick nylon film that was buffed to orient the columns in the surface's plane. The cells were filled by capillary action. A linearly polarized

---

(21) Chandrasekhar, S. *Liquid Crystals*; Cambridge: Cambridge, England, 1992; Section 3.8.

(22) Skarp, K.; Andersson, G. *Ferroelectrics Lett.* **1986**, *6*, 67.

(23) Warmerdam, T. W.; Frenkel, D.; Zijlstra, R. J. J. *Liq. Cryst.* **1988**, *3*, 1105.

5 mW HeNe laser beam was passed through the cell, and a crossed analyzer connected to a photodiode detector was used to record the electro-optic response. The X-ray diffraction analyses were carried out using unoriented helicene–dodecane mixtures contained in 1 mm diameter quartz capillary tubes and the diffractometer of NSLS beamline X10A.

Acknowledgment. The work at Columbia University was supported by NSF Grants CHE00-94723 and CHE98-02316. The work at the University of Colorado was supported by NSF MRSEC Grant DMR 98-09555. Some of the experiments used the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the DOE's Divisions of Materials Sciences and Chemical Sciences. Preliminary experiments demonstrating the switching phenomenon were carried out with the help of Dr. Daniel Krüerke and Prof. Gerd Heppke at the T. U. Berlin.[17]

CM010628O