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Ferroelectric Liquid Crystals for Nonlinear Optics: Orientation of the Disperse Red 1 Chromophore along the Ferroelectric Liquid Crystal Polar Axis[†]

David M. Walba,* Daniel J. Dyer, Teresa Sierra,[‡]
Peter L. Cobben,[§] Renfan Shao,[∥] and Noel A. Clark[∥]

Department of Chemistry and Biochemistry and
Optoelectronic Computing Systems Center
Campus Box 215, University of Colorado
Boulder, Colorado 80309-0215

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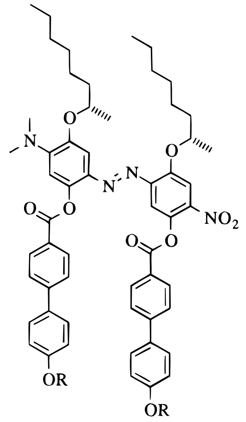
Ferroelectric liquid crystals (FLCs) are a unique state of matter possessing excellent processibility on silicon integrated circuits[1] and a thermodynamically stable polar supermolecular structure.[2] FLC thin films thus show great potential as the active organic component of fast integrated electro-optic (EO) modulators.[3] In order to realize this promise, however, FLCs with improved electronic second-order nonlinear optical (NLO) susceptibility $\chi^{(2)}$ are required, since known materials possess $\chi^{(2)}$ values too small to be useful in this application.[†,4] Herein we describe a new class of FLCs wherein for the first time the prototypical NLO chromophore *p*-nitro-*p*′-(dialkylamino)-azobenzene (the chromophore found in the NLO dye disperse red 1 (DR1)) is oriented along the polar axis. These results demonstrate that creation of FLC films with large $\chi^{(2)}$ should be possible.

Thus, while functional arrays such as the DR1 chromophore, possessing large molecular second-order susceptibility β, are easily incorporated into liquid crystal structures,[5] in all known cases the dye transition dipole, which is along the long axis of a functional array with a large aspect ratio, is oriented parallel to the liquid crystal director. Since in known FLCs the polar axis is normal to the director, conventional FLC structures containing NLO chromophores show incorrect supermolecular stereochemistry and small $\chi^{(2)}$.

In order to solve this problem, a "side-by-side dimer" structure was explored,[†,6] as illustrated by azo dyes **1a** and **1b** (Figure 1).[7] The rationale here is that the dye chromophore is forced normal to the director by rigid covalent attachment to structural components expected to orient parallel to the director, a key question being whether this structural feature is actually compatible with calamitic liquid crystallinity. In fact, both new materials possess good monotropic smectic mesogenicity as evidenced by optical polarized light microscopy and differential scanning calorimetry.[8] For these materials the LC phases often remain for days at room temperature before crystallization occurs. The linoleic acid derived polyunsaturated analog **1b** exhibits better mesogenicity,[9] showing a narrow enantiotropic A* phase. Compound **1b** also shows improved solubility in mixtures with C phase hosts relative to **1a** and was therefore chosen for further characterization as follows.



1a; R = n-Decyl; Phase sequence:
$X \leftarrow {<}25 — A^* \leftarrow 99\text{-}97 — I$

1b; R = (Z,Z)-9,12-Octadecadienyl; Phase sequence:
$X \leftarrow {<}25 — S_B \leftarrow {\cong}40 — A^* \leftarrow 74 — I$
$X — 72 \rightarrow A^* — 74 \rightarrow I$

Figure 1. Structure and phase sequences of compounds **1a** and **1b.**

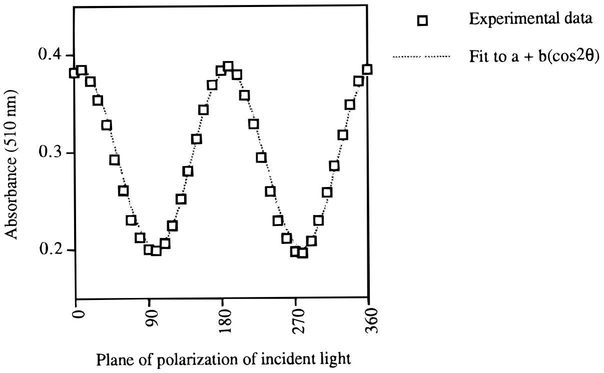


Figure 2. Absorbance at 510 nm = λ_{max} as a function of incident angle of polarized input light (0° is normal to the director) at room temperature for a 10% mixture of **1b** in a smectic A* host.[10]

The desired supermolecular structure for the A* phase of compound **1b**, wherein the director is oriented along the phenyl biphenylcarboxylate long axis and the DR1 unit is oriented at about 60° to the director, was proven experimentally by measurement of the visible light dichroism in neat samples and mixtures of compound **1b**. In the neat liquid, parallel-aligned on rubbed nylon, in the A* phase the maximum absorbance

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[‡] Current address: Quimica Orgánica, Facultad de Ciencias—ICMA, Universidad de Zaragoza—CSIC, 50009 Zaragoza, Spain.

[§] Current address: Philips Research Laboratories Eindhoven, 5656 AA, Eindhoven, The Netherlands.

[∥] Department of Physics and Optoelectronic Computing Systems Center, University of Colorado, Boulder, CO 80309-0390.

[†] Design and Synthesis of New Ferroelectric Liquid Crystals. Part 21. Previous papers in the series: Walba, D. M.; Dyer, D. J.; Cobben, P. L.; Sierra, T.; Rego, J. A.; Liberko, C. A.; Shao, R.; Clark, N. A. Ferroelectric Liquid Crystals for Nonlinear Optics Applications: Can we Really Do It? In *Thin Films for Integrated Optics Applications*; Wessels, B. W., Marder, S. R., Walba, D. M., Eds.; Materials Research Society: Pittsburgh, PA, 1995; Vol. 392, pp 157−162 and references therein.

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(3) Walba, D. M. *Science* **1995**, *270*, 250−251.

(4) (a) Walba, D. M.; Ros, M. B.; Clark, N. A.; Shao, R.; Robinson, M. G.; Liu, J.-Y.; Johnson, K. M.; Doroski, D. *J. Am. Chem. Soc.* **1991**, *113*, 5471−5474. (b) Ozaki, M.; Utsumi, M.; Gotou, T.; Morita, Y.; Daido, l. K.; Sadohara, Y.; Yoshino, K. *Ferroelectrics* **1991**, *121*, 259−274. (c) Schmitt, K.; Herr, R.-P.; Schadt, M.; Fünfschilling, J.; Buchecker, R.; Chen, X. H.; Benecke, C. *Liq. Cryst.* **1993**, *14*, 1735−1752.

(5) Interesting examples include the following: (a) Fouquey, C.; Lehn, J. M.; Malthete, J. *J. Chem. Soc., Chem. Commun.* **1987**, 1424−1426. (b) Berdagué P.; Bayle, J. P.; Ho, M.-S.; Fung, B. M. *Liq. Cryst.* **1993**, *14*, 667−674. (c) Ikeda, T.; Sasaki, T.; Ichimura, K. *Nature* **1993**, *361*, 428−430. (d) Sasaki, T.; Ikeda, T.; Ichimura, K. *J. Am. Chem. Soc.* **1994**, *116*, 625−628.

(6) While mesogens with this type of side-by-side dimer structure have not been reported previously, there is extant literature and current active interest in metal-containing FLC structures bearing side-by-side mesogenic units: Baena, M. J.; Barberá, J.; Espinet, P.; Ezcurra, A.; Ros, M. B.; Serrano, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 1899−1906.

(7) Synthesis of compounds **1** will be described separately (see supporting information). All new compounds in the routes leading to targets **1a** and **1b** as well as the mesogens themselves showed consistent ^1H and ^{13}C NMR spectra and gave satisfactory combustion analyses.

(8) The phase identification for compounds **1** was corroborated by observation of a large electroclinic effect in well-aligned samples [Andersson, G.; et al. *Appl. Phys. Lett.* **1987**, *51*, 640] for the new materials in the A* phase. This useful behavior is remarkably similar to that observed for several "monomeric" analogs of structures **1** (Walba, D. M.; Dyer, D. J.; Shao, R.; Clark, N. A.; Vohra, R. T.; More, K.; Thurmes, W. N.; Wand, M. D. *Ferroelectrics* **1993**, *148*, 435−442).

(9) Dyer, D. J.; Walba, D. M. *Chem. Mater.* **1994**, *6*, 1096−1098.

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was observed when plane-polarized input light (510 nm = λ_{max}) was oriented perpendicular to the director, consistent with the desired structure. Plots of absorbance vs input angle did not, however, show the expected $a + b\cos^2\theta$ form (where θ is the incident angle), due to the very high maximum absorbances (and nonlinear detector response) obtained even in very thin samples.

In a 10% mixture of **1b** in a room temperature A* host,[10] the absorbance as a function of incident angle is well behaved, and a dichroic ratio (absorbance parallel to $\hat{n}$/absorbance normal to $\hat{n}$) of 0.52 is observed, as indicated in Figure 2. The observed dichroic ratio of 0.52 shows that the transition moment makes an angle of 63° with the LC director.[11] This value is quite consistent with the desired supermolecular structure where the director is parallel to the phenyl biphenylcarboxylate unit.

In addition, using light from a standard microscope illuminator, neat samples of compound **1b** in the A* phase show negative birefringence. To our knowledge this is the first example of a smectic A* material with negative birefringence (the racemic material should produce a smectic A phase with negative birefringence as well), but is quite consistent with the proposed supermolecular structure since the DR1 unit has a much larger linear polarizibility for transmitted visible light than the phenyl biphenylcarboxylate units.

While neither **1a** nor **1b** shows a tilted smectic phase, compound **1b** is miscible in all proportions with a phenyl biphenylcarboxylate C phase host material,[12] affording C* mixtures at concentrations up to 60% by weight. The phase diagram of this two-component mixture is given in Figure 3 along with the measured ferroelectric polarization of the C* mixtures. As indicated in the figure, at concentrations ranging from 20% to 60% by weight of **1b**, the polarization is nicely linear with concentration, with $P_{ext} = +65$ nC/cm^2 $\cong$ 0.4 D/molecule, assuming a density of 1.1 gm/cm^3.

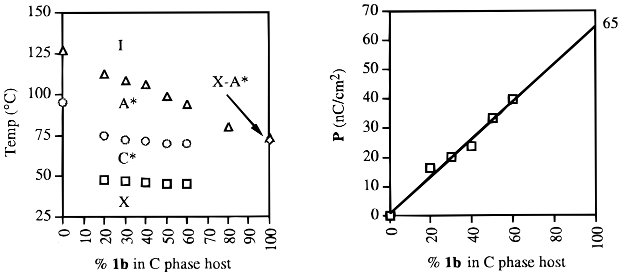
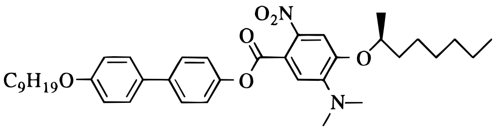


Figure 3. Two-component phase diagram (left) and maximum observed ferroelectric polarization as a function of concentration (right) for C* mixtures of **1b** in a C phase host.[12]

This result, including most importantly the *sign* of the observed ferroelectric polarization,[2] is fully consistent with the proposed polar supermolecular structure of the liquid crystal phase, suggesting a polar excess in the orientation of the DR1 unit of about 10%, assuming a net dipole moment normal to the director of about 3 D (negative at the nitro group).[13]

The relatively low degree of polar order observed in this case is not surprising, since the *p*-nitroaniline derivative **2** was also shown to have very low extrapolated ferroelectric polarization, suggesting that the dimethylamino group does not provide a high degree of polar stereocontrol when situated ortho to the (1-methylalkyl)oxy chiral tail, while the nitro group provides polar excesses of greater than 30% in the "flipped" configuration.[4a,c] In the present case the specific azo dyes **1** were chosen for ease of synthesis in these initial experiments to demonstrate the concept. Small polar excess notwithstanding, the results reported here clearly show that classic "large β" NLO chromophores can indeed be oriented along the polar axis in FLCs.



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Supporting Information Available: Full experimental details for the preparation of all new compounds in the sequence leading to compounds **1** (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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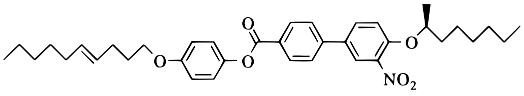
[10] The room temperature A* material (*S*)1-[[4″-[(1-methylheptyl)oxy]-3″-nitro-4′-biphenylyl]carbonyl]oxy]-4-[4(*E*)-decenyloxy]benzene (**3**) was used as host in this experiment. Details of the properties of this material will be reported elsewhere.



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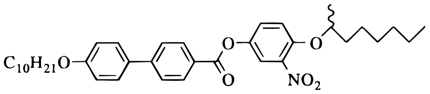
[11] For absorbers in a uniaxial liquid crystal phase such as the smectic A* the dichroic ratio gives the average angle between the transition moment and the director (θ) according to the equation $\langle\cos^2\theta\rangle = d/(d + 2)$, where d is the observed dichroic ratio: Michl, J.; Thulstrup, E. W. *Spectroscopy with Polarized Light. Solute Alignment by Photoselection, in Liquid Crystals, Polymers, and Membranes*; VCH Verlagsgesellschaft: Weinheim, 1986.

[12] The excellent C phase host material (*R,S*)-4″-[(1-methylheptyl)oxy]-3″-nitrophenyl 4′-(*n*-decyloxy)-4-biphenylcarboxylate (**4**) was used in these experiments. The (*S*) enantiomer of this material was first reported in the following: Walba, D. M.; Ros, M. B.; Clark, N. A.; Shao, R.; Johnson, K. M.; Robinson, M. G.; Liu, J. Y.; Doroski, D. Design of Ferroelectric Liquid Crystals for Electronic NLO Applications. In *Materials for Nonlinear Optics: Chemical Perspectives*; Stucky, G. D., Ed.; American Chemical Society: Washington, DC, 1991; Vol. 455, pp 484−496. The racemate is discussed in the following: Ginzburg, V. V.; Shao, R.; Clark, N. A.; Walba, D. M. Theory of chiral-racemic mixtures near the Smectic C − Smectic A transition point: Dependence of spontaneous polarization and transition temperature on enantiomeric excess. *Proc. SPIE—Int. Soc. Opt. Eng.* **1994**, *2175*, 102−107.



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[13] Gas phase MOPAC calculations using the AM1 Hamiltonian give a net dipole moment of 3.1 D along the DR1 unit for a simplified version of compounds **1** possessing the relevant structural features.