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SYNTHESIS & CHARACTERIZATION OF C2-SYMMETRIC BIPHENYLS AS NOVEL DOPANTS FOR INDUCED FERROELECTRIC LIQUID CRYSTAL PHASES

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<u>Abstract</u> We report the synthesis of novel rod-like chiral dopants bearing a C_2 -symmetric biphenyl core with a large transverse dipole moment, and the induction of a FLC phase upon doping of such compounds into a S_C host.

INTRODUCTION

Ferroelectric liquid crystals (FLC) are of considerable importance because of their application in high-speed electro-optical switching devices.¹ The switching time of a ferroelectric LCD is in the range of microseconds, and is a function of the spontaneous polarization (P_S) and the rotational viscosity (η) of the FLC. Research efforts have recently focused on the synthesis of chiral dopants with high spontaneous polarizations, which can be doped in small quantities into a S_C host mixture with low rotational viscosity and broad S_C phase range to produce fast-switching ferroelectric LCDs suitable for commercial applications.² A novel approach to the design of chiral dopants with high P_S values has been to introduce a chiral ring system with a fixed transverse dipole moment as part of the rigid core of the molecule.³⁻⁸ Such chiral ring systems effectively maximize stereo-polar coupling, and are conformationally more restricted than acyclic stereo-polar units. Following a similar design approach, we report herein the synthesis of the C₂-symmetric dopants **1a-h**, **2e** and **3e**, and the measurement of P_S values for the FLC phases obtained by doping optically active **1e** and **1h** into a S_C host.



a, R = 4-*n*-C₄H₉O; **b**, R = 4-*n*-C₅H₁₁O; **c**, R = 4-*n*-C₆H₁₃O; **d**, R = 4-*n*-C₇H₁₅O; **e**, R = 4-*n*-C₈H₁₇O; **f**, R = 4-*n*-C₉H₁₉O; **g**, R = 4-*n*-C₁₀H₂₁O; **h**, R = 4-*n*-C₁₂H₂₅O

RESULTS

Compounds 1a-h, 2e and 3e were prepared according to the route shown in Scheme I, which is derived in part from the work of Mislow.^{9,10} The conversion of 4-methoxy-2-nitroaniline (4) to methyl 2-iodo-4-methoxy-3-nitrobenzoate (6) was achieved in 23% overall yield by modification of a known procedure.¹¹ The racemic diphenic acid 7 was obtained via an Ullmann coupling, followed by hydrolysis of the corresponding diester. Resolution with (S)-methylbenzylamine gave the optically active diphenic acid 7 with an optical purity of 50% ee.¹² Following reduction with BH₃.THF, treatment of the diol 9 with 48% HBr in acetic acid resulted in the expected alcohol-to-bromide conversion along with demethylation of the 4- and 4'-methoxy groups to give 10. Reduction of the benzyl bromide groups with NaBH₃CN followed by esterification of the remaining hydroxyl groups gave the optically active 7; the racemic dopants 1a-h were obtained in similar overall yields from racemic 7. The bridged dopants 2e and 3e were both obtained from racemic 10 in 51% and 68% yield, respectively.



Cr 35 S_C 70.5 S_A 72 N 75 I

None of the C₂-symmetric dopants reported herein exhibit a liquid crystal phase (see Table I). Each compound was doped into the S_C host (\pm)-11¹³ over a range of concentrations; phase transition temperatures and solubility limits were determined by texture analysis using a Nikon Labophot-2 polarizing microscope fitted with an Instec mK1-i hot stage. The solubility of 1 in (\pm)-11 was found to be a function of the chain length of the alkoxy substituent R, leveling off at R = C₉H₁₉O with a solubility limit of nearly 20 mol%, as shown in Figure 1. By comparison, the bridged compounds **2e** and **3e** proved to be virtually insoluble in (\pm)-11, which may be due in part to the rigidity of the twisted biphenyl core imparted by the 3-membered bridge. Further experimental work showed that, at a fixed dopant concentration of 3.0 mol%, the temperature range of the S_C phase of (\pm)-11 is independent of R.

SCHEME I a



^{*a*} Reagents (yield): i, Cl₃CCH(OH)₂, NH₂OH·HCl, Na₂SO₄, H₂O, 55 $^{\circ}$ C (95%); ii, conc H₂SO₄, 95 $^{\circ}$ C (86%); iii, (1) 30% aq H₂O₂, NaOH, 25 $^{\circ}$ C, (2) AcOH (70%); iv, (1) NaNO₂, H₂SO₄, 0 $^{\circ}$ C, (2) KI, 80 $^{\circ}$ C (60%); v, MeOH, H₂SO₄, reflux (90%); vi, Cu, DMF, reflux (72%); vii, KOH, EtOH/H₂O, reflux (95%); viii, (1) (*S*)-α-methylbenzylamine (1 equiv), acetone, reflux, (2) 5% HCl; ix, 1.0 M BH₃·THF, 25 $^{\circ}$ C (94%); x, 48% HBr, AcOH, reflux (80%); xi, NaBH₃CN, HMPA, 55 $^{\circ}$ C (80%); xii, DCC, *p*-RC₆H₄CO₂H, DMAP, CH₂Cl₂, 25 $^{\circ}$ C (50-75%); xiii, NaOH, NaI, THF/H₂O, reflux (68%); xiv, Na₂S, MeOH/H₂O, reflux (90%).

Compound	R	Transition Temperature (°C)
	n-C4H9O	Cr 172 I
1b	<i>n</i> -C ₅ H ₁₁ O	Cr 152 I
1c	<i>n</i> -C ₆ H ₁₃ O	Cr 146 I
1d	<i>n</i> -C ₇ H ₁₅ O	Cr 138 I
1e	<i>n</i> -C ₈ H ₁₇ O	Cr 128 I
1 f	<i>n</i> -C9H19O	Cr 113 I
1g	<i>n</i> -C ₁₀ H ₂₁ O	Cr 119 I
1h	<i>n</i> -C ₁₂ H ₂₅ O	Cr 123 I
2e	<i>n</i> -C ₈ H ₁₇ O	Cr 182 I
3e	<i>n</i> -C ₈ H ₁₇ O	Cr 123 I

Table I Transition Temperatures for Compounds 1a-h, 2e and 3e.



FIGURE 1 Solubility limit as a function of chain length $n (R = C_n H_{2n+1}O)$ for the racemic dopant 1 in the S_C host (±)-11.

The optically active compounds 1e and 1h were each doped into (±)-11 at concentrations of 3.1 and 2.5 mol%, respectively; the mixtures were introduced into 4 μ m ITO glass cells with polyimide coating, and a square-wave AC voltage of 6 V/ μ m was applied at T_{C-A}-T = 15 °C. In each case, a Goldstone mode response characteristic of a ferroelectric liquid crystal phase was observed by polarized microscopy.¹ Tilt angle measurements at the same temperature gave values of 20 ° and 22 °, respectively. Results from control experiments confirmed that optically active **1e** and **1h** are responsible for ferroelectric induction: no Goldstone mode response was observed in the absence of dopant, nor when racemic **1e** or **1h** was used as dopant. Attempts were made at measuring the spontaneous polarization (*P_S*) of optically active **1e** and **1h** in (±)-**11** by the triangular wave method¹⁴ using a Displaytech Automated Polarization Tester. However, the spontaneous polarization of a 6 mol% mixture of either dopant in (±)-**11** proved to be too low to be measured with our instrument at any temperature below T_{C-A} . Assuming a detection limit of 0.5 nC/cm², we estimate *P*_S values for optically pure **1e** and **1h** to be < 17 nC/cm², after correcting for optical purity and extrapolating to 100 mol% concentration.

DISCUSSION

In the design of chiral dopants for induced ferroelectric liquid crystals, it is generally agreed that polar functional groups with transverse dipole moments contribute to P_S if they are sterically coupled to the asymmetric center (stereo-polar coupling), and that the magnitude of P_S is a function of the stereo-polar coupling as well as the conformational mobility of the asymmetric center.¹⁵ The novel design of chiral dopants 1-3 is based on such empirical considerations; it was envisioned that these compounds might give extrapolated P_S values comparable to those reported by Walba *et al.* for a series of (*o*-nitroalkoxy)phenyl biphenylcarboxylate S_C^* mesogens, i.e., on the order of 300-500 nC/cm².¹⁶ The results reported herein for dopants 1e and 1h in (±)-11 fall *well short* of those expectations, and may be rationalized on the basis of the Boulder model.¹⁷

According to this model, a symmetrically substituted dopant such as 1h should fit in the "lattice" of the S_C host in a transoid conformation, in which the inherently chiral biphenyl core may be relatively free to rotate about vector m, as shown in Figure 2. Such rigid rotation of the biphenyl core with respect to the two ester side-chains gives rise to *diastereomeric states* that are, in principle, different in energy, which suggests that spontaneous polarization of the induced FLC should be a function of the energy difference between any two diastereomeric states of the dopant, e.g., A and B, that contribute dipole moment vectors -P and +P in opposite directions along the C₂ axis. In the case of 1e and 1h, the difference in energy between diastereomeric states A and B depends on the relative degree of steric coupling between the ester side-chains and the substituents at the 2,2'- and 6,6'-positions, which should be almost negligible. Such weak "rotational bias" appears to be enough to trigger a ferroelectric Goldstone mode response, even though the corresponding spontaneous polarization may lie *well below* the estimated upper limit of 17 nC/cm². Support for this rationale through the use of molecular mechanics calculations is currently being sought.



FIGURE 2 Time average conformation of dopant 1h in a S_C host according to the Boulder model, and Newman-type projections along vector m of diastereometric states A and B resulting from rigid rotation of the biphenyl core about m.

CONCLUSION

The Goldstone mode response observed in voltage switching experiments on 2-3 mol% mixtures of the optically active dopants 1e and 1h in the S_C host (\pm)-11 is consistent with the expected behavior of an induced ferroelectric liquid crystal phase. To the best

of our knowledge, this is the first example of an induced FLC that is produced by doping an *inherently chiral* C₂-symmetric biphenyl compound into a S_C host. Consideration of the Boulder model provides a rationale for ferroelectric induction via 1e and 1h that is consistent with corresponding P_S values that lie below the detection limit of our instrument.

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REFERENCES AND NOTES

- J. W. Goodby, R. Blinc, N. A. Clark, S. T. Lagerwall, M. A. Osipov, S. A. Pikin, T. Sakurai, K. Yoshino, and B. Zeks, <u>Ferroelectric Liquid Crystals: Principles</u>, <u>Properties and Applications</u> (Gordon & Breach, Philadelphia, 1991).
- 2. C. Escher and R. Wingen, <u>Adv. Mat.</u>, <u>4</u>, 189 (1992).
- H. Stegemeyer, R. Meister, H.-J. Altenbach, and D. Szewczyk, <u>Liq. Cryst.</u>, <u>14</u>, 1007 (1993).
- 4. G. Scherowsky and A. Lotz, Liq. Cryst., 14, 733 (1993).
- K. Sakashita, T. Ikemoto, Y. Nakaoka, F. Terada, Y. Sako, Y. Kageyama, and K. Mori, <u>Liq. Cryst.</u>, <u>13</u>, 71 (1993).
- 6. T. Kusumoto, K.-I. Sato, K. Ogino, T. Hiyama, S. Takehara, M. Osawa, and K. Nakamura, Liq. Cryst., 14, 727 (1993).
- R. Buchecker, J. Funfschilling, and M. Schadt, <u>Mol. Cryst. Liq. Cryst.</u>, <u>213</u>, 259 (1992).
- K. Sakaguchi, T. Kitamura, Y. Shiomi, M. Koden, and T. Kuratate, <u>Chem. Lett.</u>, 1383 (1991).
- F. A. McGinn, A. K. Lazarus, M. Siegel, J. E. Ricci, and K. Mislow, <u>J. Am. Chem.</u> <u>Soc.</u>, 80, 476 (1958).
- 10. Each compound was fully characterized by ¹H, ¹³C NMR spectroscopy and mass spectrometry, and gave satisfactory elemental analysis.
- 11. V. H. Cassebaum, J. Prakt. Chem., 23, 301 (1964).
- 12. The optical purity of 7 as the diester 8 was determined by ¹H NMR spectroscopy (200 MHz, CDCl₃) using Eu(hfc)₃ (3 equiv) as chiral shift reagent.
- 13. P. Keller, Ferroelectrics, 58, 3 (1984).
- K. Miyasato, S. Abe, H. Takezoe, A. Fukuda, and E. Kuze, <u>Jpn. J. Appl. Phys.</u>, <u>22</u>, L661 (1983).
- S. T. Lagerwall, B. Otterholm, and K. Skarp, <u>Mol. Cryst. Liq. Cryst.</u>, <u>152</u>, 503 (1987).
- D. M. Walba, M. B. Ros, N. A. Clark, R. Shao, K. M. Johnson, M. G. Robinson, J. Y. Liu, and D. Doroski, <u>Mol. Cryst. Liq. Cryst.</u>, <u>198</u>, 51 (1991).
- D. M. Walba, S. C. Slater, W. N. Thurmes, N. A. Clark, M. A. Handschy, and F. Supon, J. Am. Chem. Soc., 108, 5210 (1986).