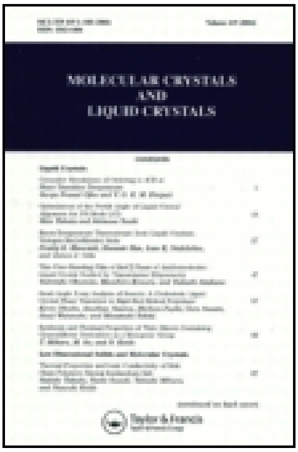

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Synthesis and Characterization of C_2-Symmetric Biphenyls as Novel Dopants for Induced Ferroelectric Liquid Crystal Phases

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SYNTHESIS & CHARACTERIZATION OF C_2-SYMMETRIC BIPHENYLS AS NOVEL DOPANTS FOR INDUCED FERROELECTRIC LIQUID CRYSTAL PHASES

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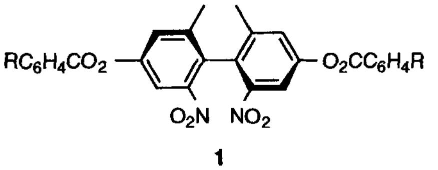
Abstract We report the synthesis of novel rod-like chiral dopants bearing a C_2-symmetric biphenyl core with a large transverse dipole moment, and the induction of a FLC phase upon doping of such compounds into a S_C host.

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 C_2-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.



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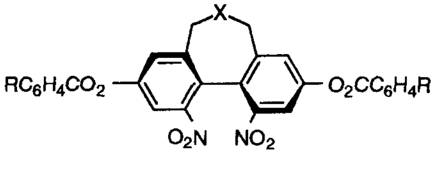
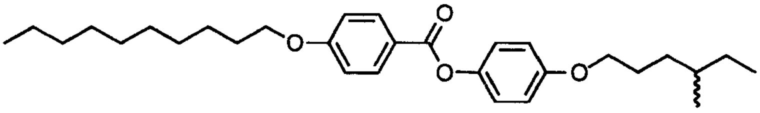


2, X = O; **3**, X = S

a, R = 4-*n*-C_4H_9O; **b**, R = 4-*n*-$C_5H_{11}O$; **c**, R = 4-*n*-$C_6H_{13}O$; **d**, R = 4-*n*-$C_7H_{15}O$; **e**, R = 4-*n*-$C_8H_{17}O$; **f**, R = 4-*n*-$C_9H_{19}O$; **g**, R = 4-*n*-$C_{10}H_{21}O$; **h**, R = 4-*n*-$C_{12}H_{25}O$

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 BH_3·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 $NaBH_3CN$ followed by esterification of the remaining hydroxyl groups gave the optically active dopants **1e** and **1h** in 40% and 50% overall yield, respectively, from 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.

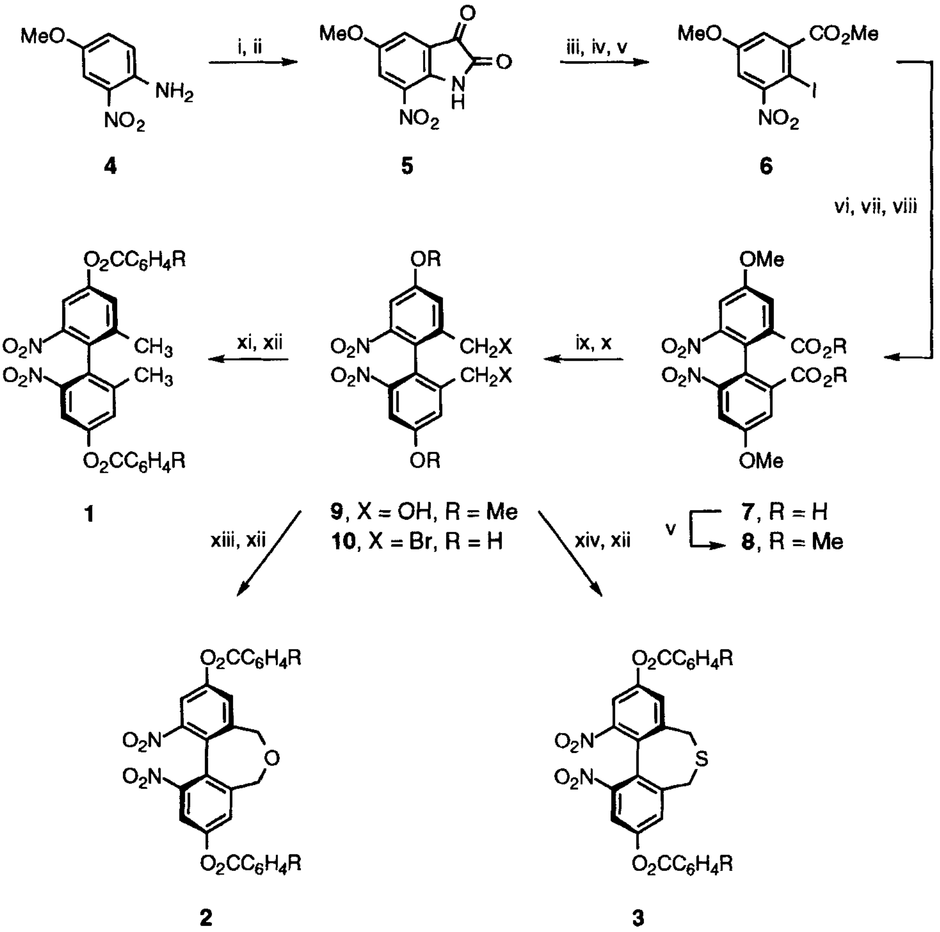


(±)-**11**

Cr 35 S_C 70.5 S_A 72 N 75 I

None of the C_2-symmetric dopants reported herein exhibit a liquid crystal phase (see Table I). Each compound was doped into the S_C host (±)-**11**[13] 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 (±)-**11** was found to be a function of the chain length of the alkoxy substituent R, leveling off at R = $C_9H_{19}O$ 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 (±)-**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 (±)-**11** is independent of R.

SCHEME I[a]



[a] Reagents (yield): i, $Cl_3CCH(OH)_2$, $NH_2OH\cdot HCl$, Na_2SO_4, H_2O, 55 °C (95%); ii, conc H_2SO_4, 95 °C (86%); iii, (1) 30% aq H_2O_2, NaOH, 25 °C, (2) AcOH (70%); iv, (1) $NaNO_2$, H_2SO_4, 0 °C, (2) KI, 80 °C (60%); v, MeOH, H_2SO_4, reflux (90%); vi, Cu, DMF, reflux (72%); vii, KOH, EtOH/H_2O, reflux (95%); viii, (1) (*S*)-α-methylbenzylamine (1 equiv), acetone, reflux, (2) 5% HCl; ix, 1.0 M $BH_3\cdot THF$, 25 °C (94%); x, 48% HBr, AcOH, reflux (80%); xi, $NaBH_3CN$, HMPA, 55 °C (80%); xii, DCC, *p*-$RC_6H_4CO_2H$, DMAP, CH_2Cl_2, 25 °C (50-75%); xiii, NaOH, NaI, THF/H_2O, reflux (68%); xiv, Na_2S, MeOH/H_2O, reflux (90%).

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

Compound	R	Transition Temperature (°C)
1a	n-C_4H_9O	Cr 172 I
1b	n-$C_5H_{11}O$	Cr 152 I
1c	n-$C_6H_{13}O$	Cr 146 I
1d	n-$C_7H_{15}O$	Cr 138 I
1e	n-$C_8H_{17}O$	Cr 128 I
1f	n-$C_9H_{19}O$	Cr 113 I
1g	n-$C_{10}H_{21}O$	Cr 119 I
1h	n-$C_{12}H_{25}O$	Cr 123 I
2e	n-$C_8H_{17}O$	Cr 182 I
3e	n-$C_8H_{17}O$	Cr 123 I

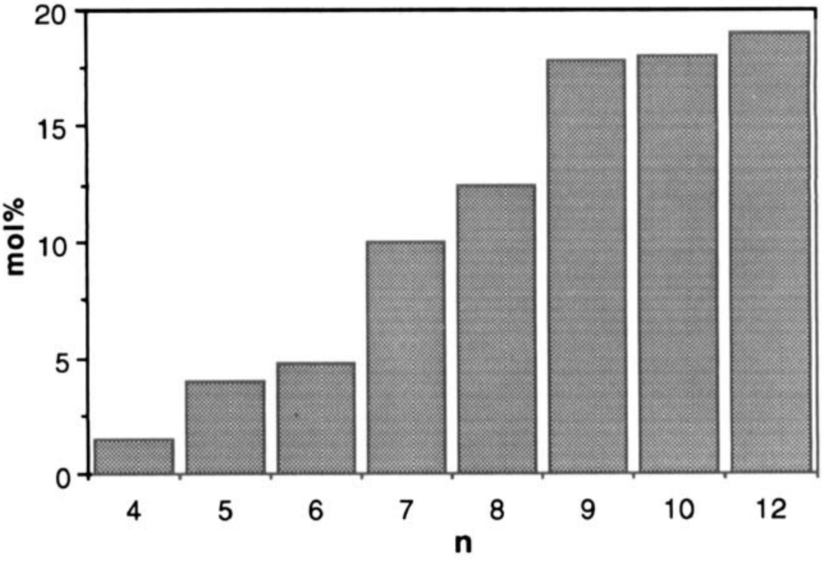


FIGURE 1 Solubility limit as a function of chain length **n** (R = $C_nH_{2n+1}O$) for the racemic dopant **1** in the S_C host (±)-**11**.

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 μm ITO glass cells with polyimide coating, and a square-wave AC voltage of 6 V/μm was applied at $T_{C\text{-}A} - T = 15$ °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 method[14] 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 $T_{C\text{-}A}$. Assuming a detection limit of 0.5 nC/cm^2, we estimate P_S values for optically pure **1e** and **1h** to be < 17 nC/cm^2, 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/cm^2.[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 $\boldsymbol{m}$, 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 $-\boldsymbol{P}$ and $+\boldsymbol{P}$ in opposite directions along the C_2 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/cm^2. Support for this rationale through the use of molecular mechanics calculations is currently being sought.

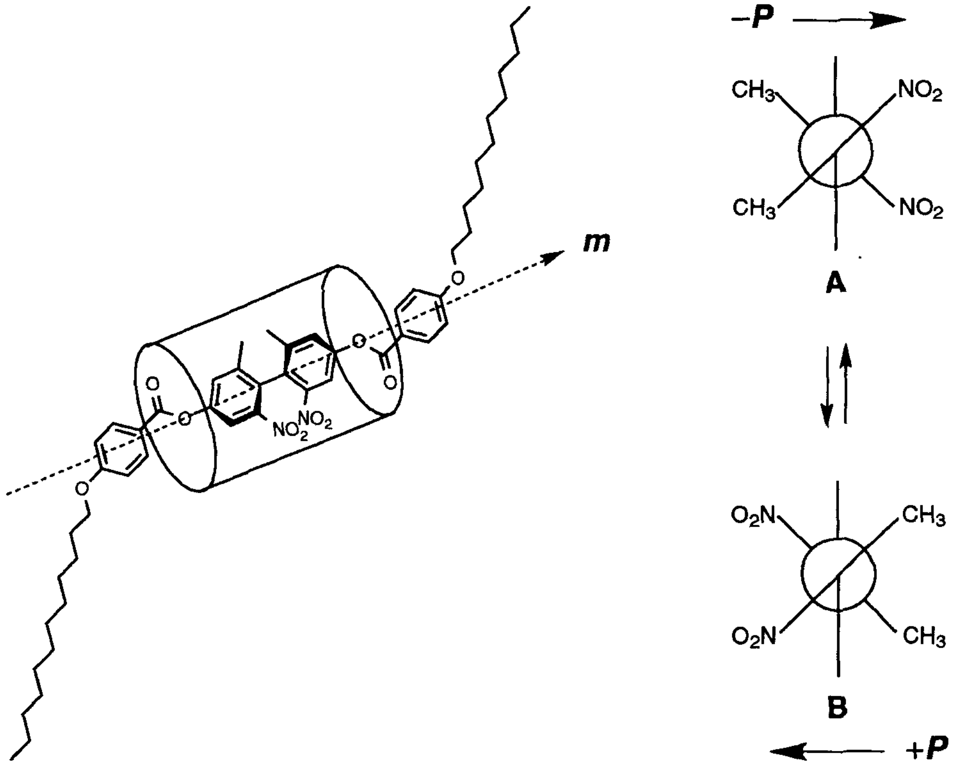


FIGURE 2 Time average conformation of dopant **1h** in a S_C host according to the Boulder model, and Newman-type projections along vector ***m*** of diastereomeric states **A** and **B** resulting from rigid rotation of the biphenyl core about ***m*** .

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 (±)-**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* C_2-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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