

Effects of Desymmetrization on Thiophene-Based Bent-Rod Mesogens

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The synthesis and characterization of various thiophene-based bent-rod liquid crystals are reported, and the effects of varying lateral dipole and core desymmetrization upon mesophase behavior are described. Incorporation of desymmetrized core **7** into the molecular framework was found to have very different consequences depending upon whether *n*-alkoxy or tetracatenar-type end groups were used. Tetracatenar-type mesogens **8–11** were found to be significantly less mesogenic than the previously reported symmetric series **3**. When symmetric straight-chain compounds **13–17** and unsymmetric straight-chain compounds **18–21** were investigated, however, the desymmetrized core was found to give rise to mesophases with much broader temperature ranges. Variable temperature X-ray diffraction of these compounds suggests the formation of antiparallel dimers of molecules within the liquid crystal phase, and this may explain the relatively stable mesophases formed by these compounds and their incompatibility with chiral induction. The effects of altering the lateral substituents were also explored, and 3,4-difluorothiophene-based compounds **24–27** were found to exhibit broad nematic mesophases.

Introduction

The search for molecules that possess rigid bent-rod shapes and are capable of forming liquid crystal phases has been an area of extensive investigation in the past decade.¹ This is largely due to the numerous reports of novel mesogenic phases (banana phases) exhibited by certain bent-rod compounds, most notably switchable antiferroelectric and ferroelectric phases.² These phases form domains of bulk polarization due to the spontaneous adoption of chiral structures by the inherently achiral molecules.³ The decrease in symmetry caused by the bent shape of these molecules is central to the formation and structure of the phases themselves, as nearest-neighbor interactions and packing considerations for such mesogens become more complex than in the case of conventional calamitic molecules. However, despite the large number of molecules studied, the structure–property relationships that govern these phases still remain largely unelucidated.

One long-standing interest of our group has been in utilizing the shape anisotropy of unconventional

mesogens to create mesophases with polar order.⁴ Bent-rod mesogens which possess a large laterally directed dipole might be expected to display polar phases due to the combination of dipolar forces and packing considerations arising from the shape anisotropy of the molecules. We have previously reported the synthesis of a number of bent-rods based on 2,5-disubstituted-3,4-dicyanothiophenes (Figure 1).^{5,6} The 2,5-thienyl linkage of this design imparts a moderate bend angle of 154° and results in mesophases with greater stability than mesogens with similar architectures and a more pronounced bend. We have also previously demonstrated that increasing the aspect ratio through the addition of bridging ethynyl moieties promotes mesomorphism in these compounds. The incorporation of nitrile groups in the 3,4-positions of the thiophene ring imparts a very significant lateral dipole and results in a head-to-head antiparallel arrangement of molecules. This has been evidenced by the previously reported single-crystal structure of a model compound **14** (Figure 1) and by variable temperature 2-D X-ray diffraction and exciton coupling studies of the Col_H phase of a structurally similar hexacatenar derivative.⁷ The combination of bent shape and large lateral dipole should hinder rotation about the molecular long axis, thereby encour-

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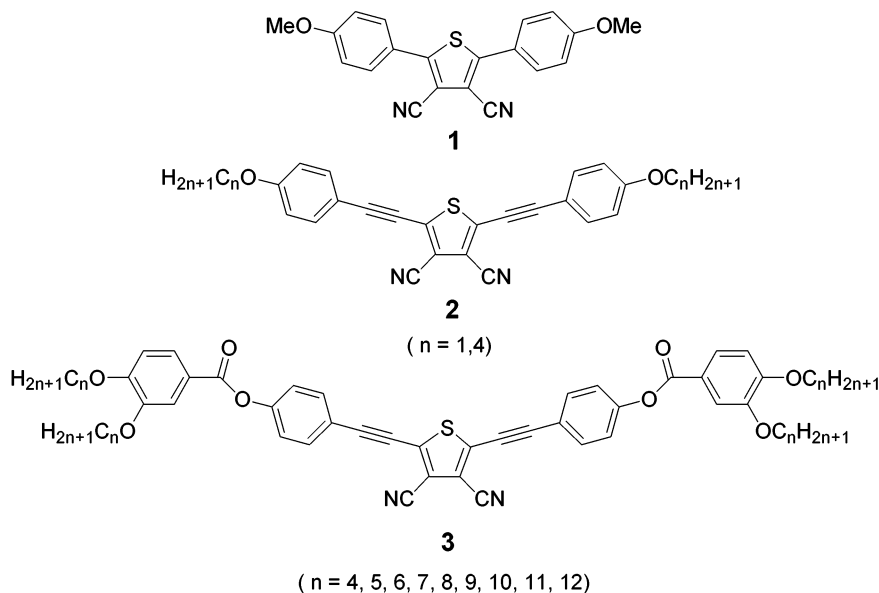


Figure 1. Previously reported 3,4-dicyanothiophene-based mesogens.

aging the formation of mesophases with a biaxial component, in which there is preferential alignment perpendicular to the long axes of the molecules. Furthermore, it has been predicted that bent molecules with large lateral dipoles should exhibit a significant flexoelectric effect, where the physical manipulation (bending) of a thin film results in bulk polarity within the material.⁸

Our previous efforts focused on the synthesis and investigation of only a few straight-chain derivatives of type **2**, followed by numerous tetracatenars of general type **3** (Figure 1). Compounds **3** were designed with the 3,4-dialkoxybenzoate terminal groups due to the diverse range of mesophases that tetracatenar ("four-chain") compounds exhibit in both traditional straight rod⁹ and metallomesogen¹⁰ systems. Indeed, compounds **3** were found to possess enantiotropic nematic, smectic C, and columnar hexagonal phases, depending on the length of the alkoxy side chains.⁶ The observation of SmC phases was encouraging, as this represents a step toward the realization of polar order. We were also pleased to observe nematic phases that display exclusively two-brush disclinations by polarized microscopy, an indication that these may be thermotropic biaxial-nematic phases.¹¹ The conclusive demonstration of biaxiality in thermotropic nematics has proven challenging, however, and further studies are necessary to elucidate the nature of the above-mentioned nematic phases.

Herein we report our continuing efforts with this class of mesogens, particularly our investigation into the effects of desymmetrization of the molecular core upon mesophase behavior. Lowering the symmetry of the mesogens was expected to suppress crystallization by

increasing the entropic cost of organization in the crystalline phase, thereby leading to lower melting temperatures and broader mesophases. Desymmetrized molecules might additionally lead to the frustration of lamellar superstructures, resulting in re-entrant nematic phases at lower temperatures and with higher order, providing further impetus for the formation of thermotropic biaxial nematic phases.

Results and Discussion

Synthesis. A number of thiophene-based mesogens were synthesized and studied (Schemes 1 and 2). The synthesis of symmetric core **12** has been previously reported.⁶ Our idea of a desymmetrized core took shape as compound **7** in which one of the acetylenic bridges has been removed. Compound **4** is prepared by palladium-catalyzed cross-coupling of 4-phenylmethoxyphenyl boronic acid with the reactive 2-position of tetrabromothiophene,¹² followed by chromatographic separation of the product of 2,5-diaddition. Chemo-selective Sonogashira cross-coupling¹³ at the 2-position of bromine of **4** with 4-phenylmethoxyphenylacetylene affords **5** in good yield, which can be converted to **6** by subsequent cyanation of the 3,4-positions of the thiophene ring with copper(I) cyanide.¹⁴ The two benzyl-protecting groups can be removed with BBr₃ in dichloromethane at low temperature, providing the desired desymmetrized core **7**. Esterification of **7** by activation of the appropriate 3,4-dialkoxyphenyl carboxylic acid with 4-(dimethylamino)pyridine and diisopropylcarbodiimide yields desymmetrized tetracatenar mesogens **8–11**. Etherification of unsymmetric core **7** and symmetric core **12** were carried out in the presence of PPh₃ and diethylazodicarboxylate, yielding straight-chain derivatives **13–21**. Utilization of these conditions not only drives the reaction at room temperature by the formation of the exceedingly stable byproduct tri-

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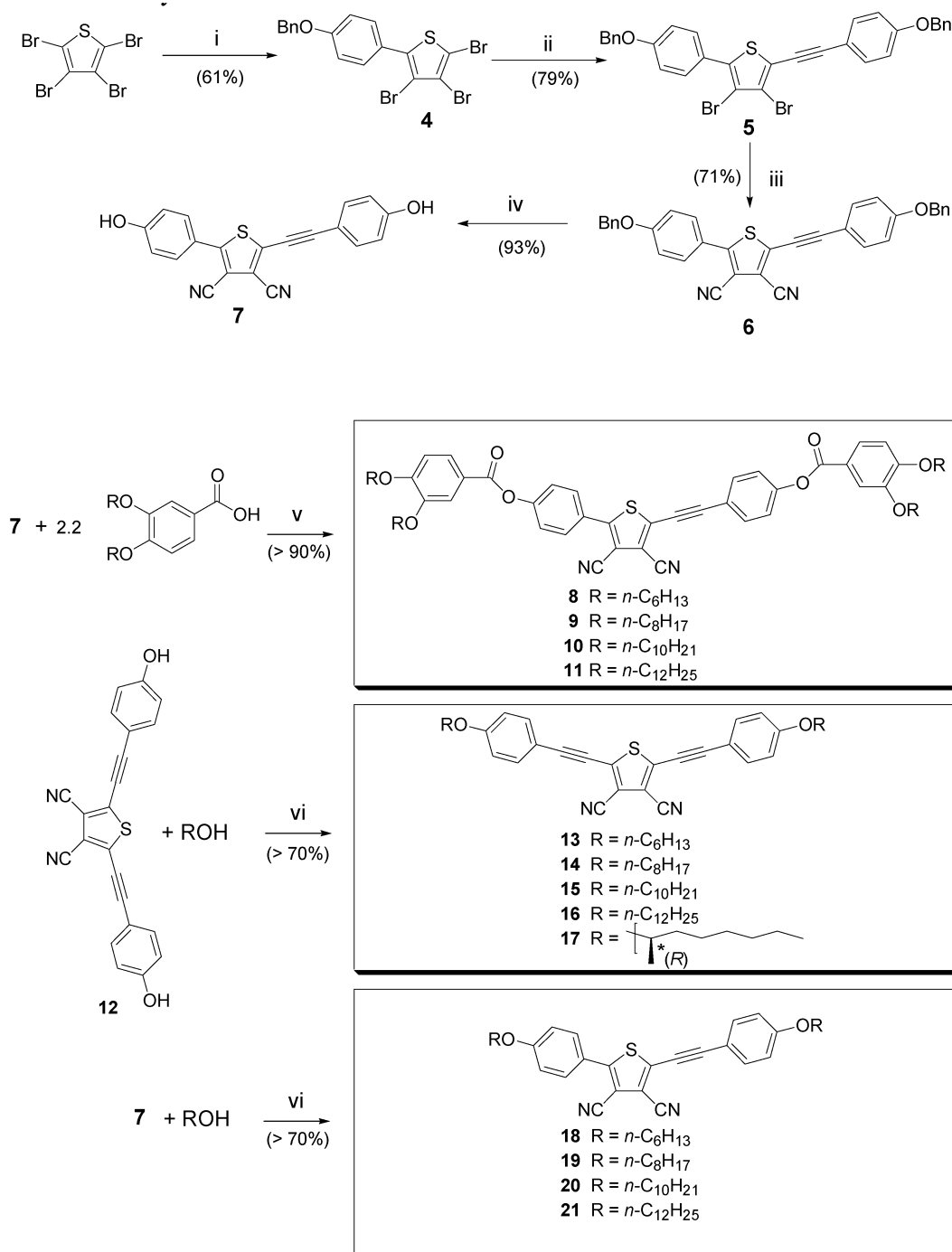
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Scheme 1. Synthesis



(i) p -BnOPhB(OH)₂, Pd(PPh₃)₄, Na₂CO₃, EtOH, H₂O, toluene, reflux. (ii) p -BnOPhCCH, Pd(PPh₃)₂Cl₂, CuI, i -Pr₂NH, toluene, r.t. (iii) CuCN (6 equiv), CuI (2 equiv), DMF, reflux. (iv) BBr₃, H₂O, DCM, -10 °C. (v) Diisopropylcarbodiimide, DMAP, DCM. (vi) PPh₃, DEAD, THF, r.t.

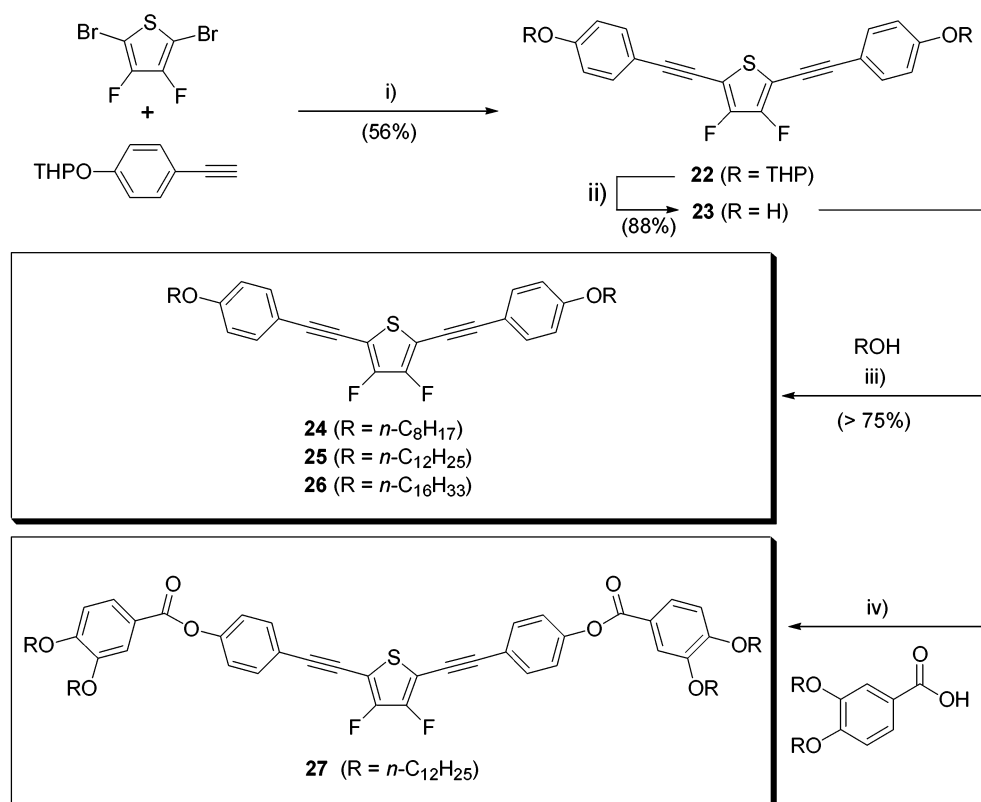
phenylphosphine oxide but also allows for the addition of chiral alcohols with a complete inversion of stereochemistry.¹⁵ Chiral derivative **17** is therefore accessible by the reaction of **12** with (*s*)-(+)-2-octanol. Similar synthetic strategies allow for the synthesis of 3,4-difluorothiophene derivatives **24–27** (Scheme 2) from starting material 2,5-dibromo-3,4-difluorothiophene, which is available as previously published in three steps from tetrabromothiophene.¹⁶

Phase Behavior. The phase behavior of the mesogens studied is listed in Table 1. Unsymmetric tetracatenar derivatives **10** and **11**, possessing long (C₁₀ and C₁₂) aliphatic side chains, exhibit Col_H phases as identified by polarized microscopy and X-ray diffraction. The shorter chain derivatives do not exhibit any mesomorphism. This is in marked contrast to the previously studied symmetric tetracatenars **3** in which nematic, SmC, and Col_H phases are observed depending on the

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Scheme 2. Synthesis of 3,4-Difluorothiophene-Based Bent-Rod Mesogens



(i) Pd(Ph₃)₂Cl₂, CuI, *i*-Pr₂NH, toluene. (ii) AcOH, THF, H₂O, 45 °C. (iii) PPh₃, DEAD, THF. (iv) Diisopropylcarbodiimide, DMAP, CH₂Cl₂.

length of the side chains. In the case of these tetracatenar systems, the effect of desymmetrization is to discourage the formation of nematic and lamellar mesophases without significantly affecting the stability of the crystalline phase.

Though we had previously studied a few very short straight-chain derivatives **2** (Figure 1), the longer chain analogues had not been explored. Our current studies of 2,5-bis[4-(*n*-alkyloxy)phenylethynyl]-3,4-dicyanothiophenes **13–16** reveal both enantiotropic nematic and smectic C phases, depending on the length of the side chains. Chiral analogue **17** is not liquid crystalline. The smectic C phases of **14** and **15** exhibit focal-conic textures by polarized microscopy (Figure 2), while the smectic C phase of compound **16** exhibits a Schlieren-type texture. Well-ordered homogeneous alignment (parallel to the slide surface) of the nematic phases of compounds **14** and **15** can be induced on slides possessing a rubbed polyimide alignment layer, but homeotropic (perpendicular to the slide) alignment could not be achieved.

Desymmetrized straight-chain compounds **18–21** exhibit similar mesophases with alignment behavior and textural features identical to symmetric compounds **13–17**, but in all cases both the clearing and crystallization temperatures are significantly depressed when compared to their symmetric analogues. In such straight-chain compounds the incorporation of a desymmetrized core results in broader mesophases due to destabilization of the crystal phases. It is interesting to note that this is in direct contrast to the two series of tetracatenar compounds discussed above in which desymmetrization had a deleterious effect upon liquid-crystalline behavior.

The incorporation of 3,4-difluoro substituents into the molecular core imparts a smaller lateral dipole to the resulting mesogens and resulted in the formation of enantiotropic nematic phases in both the straight-chain compounds **24–26** and the tetracatenar compound **27**. Despite the rather broad temperature ranges of the nematic phases, no lamellar phases were observed for these compounds. This is particularly striking in the case of the straight-chain derivatives, whose 3,4-dicyanothiophene analogues displayed broad, enantiotropic tilted lamellar phases.

XRD Studies. Variable temperature X-ray diffraction studies were performed for the lamellar and columnar phases of each compound (Table 2). The Col_H phases of compounds **10–11** are characterized by the observation of sharp (100), (110), and (200) peaks in the low-angle region as well as broad reflection centered at 4.4 Å. The SmC phases of compounds **14–16** and **19–21** are characterized by a large sharp (100) peak at low angle corresponding to the interlayer spacing as well as a broad reflection centered at 4.4 Å. Analysis of the higher angle region reveals an antiparallel (dimerized) packing of the molecules in each of the smectic C and Col_H phases, as evidenced by an extra intracore diffuse diffraction peak from 6.5 to 7.5 Å. We have observed this feature extensively for half-disk mesogens in columnar phases that similarly have antiparallel dimer correlations.¹⁷

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Table 1. Phase Behavior of Thiophene-Based Bent Rods^a

Compound	n	Behavior
8	6	$K \xrightleftharpoons[107.9 (-41.1)]{139.9 (44.4)} I$
9	8	$K \xrightleftharpoons[104.1 (-42.1)]{121.7 (45.5)} I$
10	10	$K \xrightleftharpoons[90.8 (-37.3)]{117.5 (53.7)} I$ $K \xrightarrow{90.8 (-37.3)} Cub^b \xleftarrow{103.7 (-0.8)} Col_H \xleftarrow{110.9 (-3.2)} I$
11	12	$K \xrightleftharpoons[83.3 (-54.6)]{112.7 (54.5)} Col_H \xrightleftharpoons[120.1 (-4.4)]{121.5 (4.4)} I$
13	6	$K \xrightleftharpoons[136.2 (-16.5)]{144.9 (22.7)} I$
14	8	$K_1 \xrightarrow{65.8 (12.1)} K_2 \xrightarrow{99.6 (31.7)} N \xrightleftharpoons[126.6 (-1.3)]{127.4 (1.2)} I$ $K_1 \xleftarrow{74.6 (-36.9)} SmC \xleftarrow{92.4 (-0.7)} N$
15	10	$K \xrightleftharpoons[81.7 (-43.8)]{89.0 (45.2)} SmC \xrightleftharpoons[109.8 (-1.7)]{111.3 (1.9)} N \xrightleftharpoons[120.2 (-1.9)]{121.7 (1.9)} I$
16	12	$K \xrightleftharpoons[82.8 (-46.1)]{95.7 (45.5)} SmC \xrightleftharpoons[111.3 (-5.4)]{114.4 (6.8)} I$
18	6	$K \xrightleftharpoons[78.9 (-28.5)]{99.2 (41.3)} I$ $K \xrightarrow{78.9 (-28.5)} N \xleftarrow{86.8 (-0.7)} I$
19	8	$K \xrightleftharpoons[37.2 (26.8)]{73.0 (29.6)} SmC \xrightleftharpoons[79.1 (-0.4)]{80.6 (0.4)} N \xrightleftharpoons[94.1 (-1.7)]{95.4 (1.5)} I$
20	10	$K \xrightleftharpoons[31.2 (15.3)]{65.5 (20.9)} SmC \xrightleftharpoons[95.3 (-0.8)]{95.5 (0.8)} N \xrightleftharpoons[97.9 (-2.7)]{98.8 (2.5)} I$
21	12	$K \xrightleftharpoons[35.4 (-18.8)]{69.4 (22.7)} SmC \xrightleftharpoons[98.5 (-6.2)]{100.0 (6.9)} I$
24	8	$K \xrightleftharpoons[53.8 (-37.8)]{65.2 (38.9)} N \xrightleftharpoons[107.0 (-1.5)]{109.7 (1.4)} I$
25	12	$K \xrightleftharpoons[55.0 (-58.4)]{68.8 (78.8)} N \xrightleftharpoons[96.0 (-2.0)]{98.8 (2.0)} I$
26	16	$K \xrightleftharpoons[72.1 (-92.0)]{81.0 (107.3)} N \xrightleftharpoons[89.6 (-2.6)]{92.4 (2.5)} I$
27	8	$K \xrightleftharpoons[100.8 (-58.3)]{118.0 (53.1)} N \xrightleftharpoons[119.0 (-1.2)]{121.5 (1.0)} I$

^a The transition temperatures (°C) and enthalpies (in parentheses, kJ/mol) were determined by DSC (10 °C/min) and are given above and below the arrows. *K*, *K*₁, and *K*₂ indicate crystal phases, and *SmC*, *N*, and *I* indicate smectic C, nematic, and isotropic phases, respectively. ^b This phase was identified by the appearance of a pseudo-isotropic texture below the *Col_H* phase. We were unable to observe this thermodynamically unstable monotropic phase by X-ray diffraction due to crystallization, though the phase transition was clearly visible by DSC at the 10 °C/min scan rate.

Collecting data over several temperatures, one finds that the layer spacings of the smectic C phases tend to increase with temperature (Figure 3). This suggests that the tilt angle decreases as the temperature increases,

as is expected for tilted smectic phases.¹⁸ Precise measurement of the tilt angles of the *SmC* phases of the straight-chain compounds **14–16** and **19–21** could not be achieved due to the difficulty of obtaining

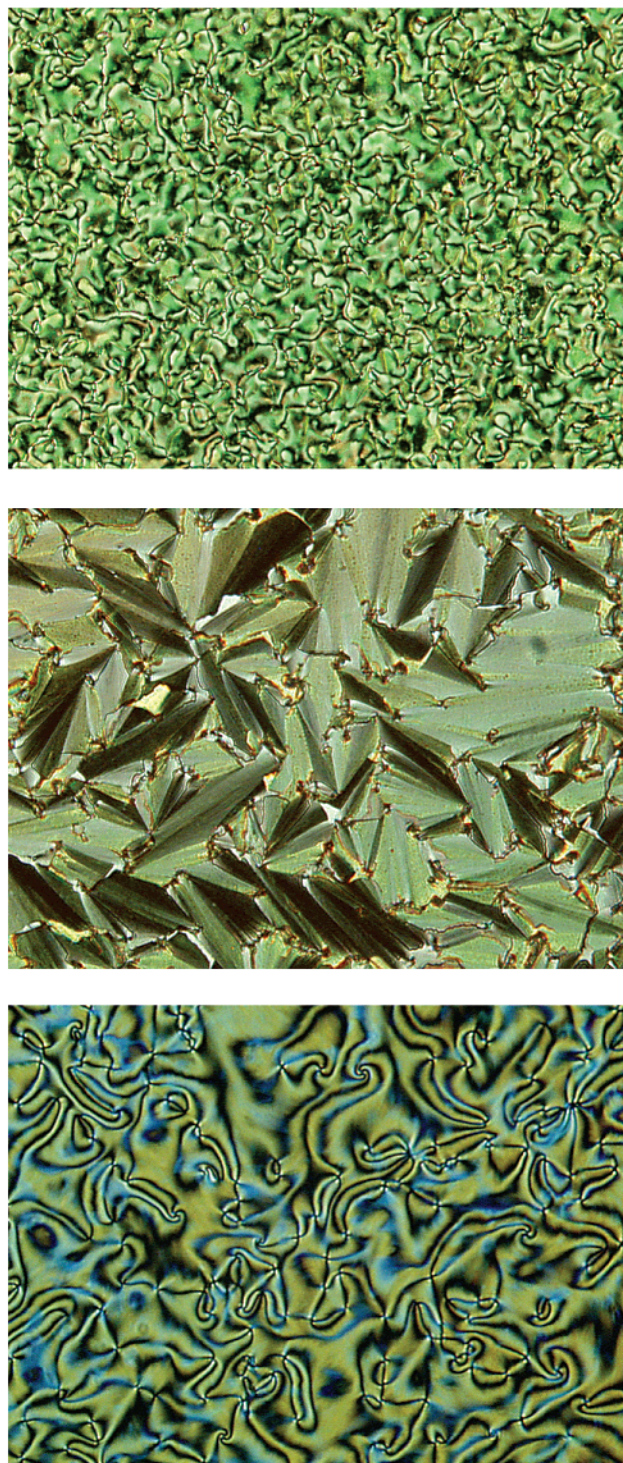


Figure 2. Microphotographs of the nematic Schlieren texture of **15** at 117 °C (100 \times) (top), the broken focal conic texture of **15** at 101 °C (200 \times) (middle), and the SmC schlieren texture of **21** at 98 °C (320 \times). Samples were sandwiched between untreated glass slides and viewed through crossed polarizers.

magnetically well-aligned samples of these compounds. Two-dimensional variable temperature X-ray analysis of a reasonably well-aligned sample of compound **14** suggests that the tilt angle is in the range of 5–10°, measured as the deviation from orthogonality between

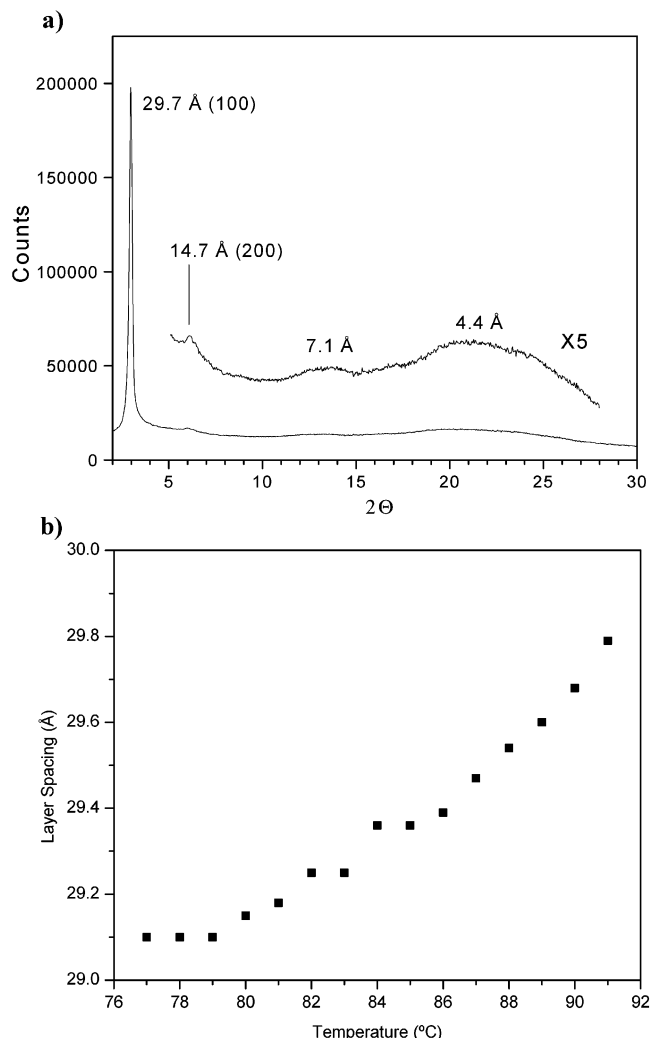


Figure 3. (a) Variable temperature powder diffraction X-ray of the SmC phase of compound **14** at 80 °C. A distinct halo is visible at 7.1 Å, corresponding to the distance between repeat units in an antiparallel arrangement of nearest neighbors. Also visible at higher angle (4.4 Å) is the broad halo corresponding to the interaction between the fluid aliphatic side chains. (b) Temperature dependence of the layer spacing (100) peak, suggesting that the tilt angle of the molecules increases with decreasing temperature.

the line described by the centers of the diffuse halos of the liquid side chains relative to the line described by the centers of the (100) reflections of the layer spacing (see Supporting Information). This is a relatively small value when compared to those of previously studied SmC phases of symmetric tetracatenar compounds **3**, which have tilt angles of up to 53°. The larger tilt angles of the tetracatenars may result from the conformational mobility of the ester group combined with the tendency of these molecules to stack, which leads to the formation of columnar phases in long-chain derivatives.

The formation of antiparallel dimers may explain the absence of mesomorphism in the chiral analogue **17**, as efficient packing within an antiparallel arrangement of molecules is sterically disfavored by the incorporation of chiral side chains. The addition of chiral side chains to mesogens typically reduces the stability of the resulting mesophases¹⁹ due to the steric interference of the chiral groups with efficient molecular packing, but this effect is extremely exaggerated in molecules that tend

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Table 2. XRD for Compounds 10, 11, 14–16, and 19–21

compd	meso-phase	lattice constant (Å)	spacing obsd (Å)	Miller indices	Å (calcd)	halos obsd (Å)
10	Col _{hd} at 100 °C	40.5	35.1	100		7.0–7.5
			20.6	110	(20.3)	3.5–7.0
			18.0	200	(17.5)	
11	Col _{hd} at 111 °C	42.7	37.0	100		7.0–7.5
			22.9	110	(21.4)	3.5–7.0
			19.4	200	(18.5)	
14	SmC at 85 °C		29.7			7.0–7.5
15	SmC at 98 °C					3.5–7.0
			32.5			7.0–7.5
16	SmC at 100 °C		33.1			3.5–7.0
19	SmC at 65 °C		29.8			7.0–7.5
						3.5–7.0
20	SmC at 72 °C		32.7			7.0–7.5
						3.5–7.0
21	SmC at 60 °C		33.4			3.5–7.0
						3.5–7.0

to pack in an antiparallel fashion. Such an organization positions the methyl groups of neighboring molecules toward each other rather than away from each other as is the case in a typical chiral mesophase (Figure 4). Compound **17** melts to the isotropic at 58 °C, is not mesomorphic on cooling, and crystallizes only after several minutes at room temperature. This result is consistent with previous results from our group, demonstrating the incompatibility of similar compounds with chiral induction.⁶

Summary and Conclusions

We have synthesized a number of thiophene-based bent-rod liquid crystals with large lateral dipoles. The effects of desymmetrization of the mesogenic core upon phase behavior has been probed, and it was found that the effects are dependent upon the end groups employed. In the case of tetracatenar systems, desymmetrization does not significantly discourage crystal-

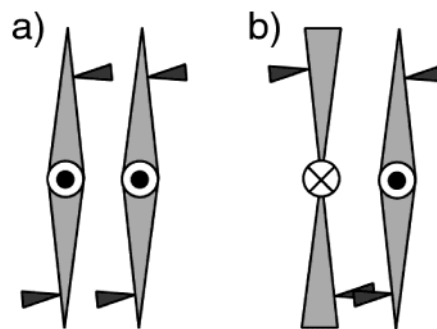


Figure 4. (a) Parallel arrangement of chiral mesogens allows chiral groups to all face in one direction. (b) Antiparallel arrangement of mesogens forces one pair of chiral groups into sterically unfavorable contact.

lization, but the mesophases are clearly destabilized, leading to complete suppression of mesomorphism in compounds **8** and **9** and much narrower liquid-crystal phases for the desymmetrized compounds **10** and **11**. The opposite proves to be the case for the straight-chain analogues **13–16** and **18–21**, wherein desymmetrization leads to significantly lower crystallization temperatures, resulting in much broader mesophases in the unsymmetric than in the symmetric compounds. The Col_H phases of compounds **10** and **11** and the smectic C phases of **14–16** and **19–21** exhibit an antiparallel arrangement of molecules, as evidenced by the appearance of a peak at 6.5–7.5 Å in the variable temperature X-ray diffraction patterns. The tilt angles of the SmC phases of straight-chain compounds **14–16** and **19–21** are temperature dependent and appear to be significantly lower than those previously measured for tetracatenars **3**, which may explain their compatibility with desymmetrization of the mesogenic core.

Supporting Information Available: Figure of an X-ray diffraction of a sample of the SmC phase of **14** and experimental data on the studied compounds (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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