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Ferroelectric Dimeric Liquid Crystals with a Chiral Flexible Spacer

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The synthesis and ferroelectric properties of a new family of mesogenic chiral compounds are described. These compounds are dimers consisting of two mesogenic units joined by a flexible spacer, namely, the (*R*)-(+)-3-methyladipoyl group. Seven different mesogenic units derived from ester, thioester, biphenyl, and naphthalene groups were introduced. The effects of the different central cores in the mesogenic units of the dimer on the transition temperature and mesophase polymorphism are investigated. Some of the compounds showed a S_C* mesophase. The spontaneous polarization (P_s) values were very small (<0.1 nC/cm^2), but this phase proved to be ferroelectric since it shows electrooptical switching with a response time $\tau = 1$ ms.

Introduction

Previously, we reported the mesogenic properties of two new series of dimeric compounds incorporating a chiral center in a flexible spacer which joins two identical mesogenic units.[1,2] In both cases we had difficulty in studying their physical properties due to their thermal and/or chemical instability. As a continuation of this work and in order to obtain compounds with the same structure but thermally and chemically stable, we synthesized and studied eight new compounds consisting of two identical mesogenic units joined by the (*R*)-(+)-3-methyladipoyl group, with the general structure A (Chart I). In these mesogenic units we introduced the ester bridge which is known to be strong enough to resist high temperatures and electric fields without breaking.[3] We introduced different mesogenic units, changing the orientation of the ester bond in order to establish the relationship between structure and mesogenic properties in this type of compound.

All the compounds, with the exception of I, show mesomorphic behavior, which was studied by means of optical microscopy and differential scanning calorimetry.

The mesophases were identified by observation of the textures by optical microscopy and some were confirmed by X-ray diffraction. Some physical studies of these compounds were carried out in order to establish their ferroelectric character. These studies deal with the determination of their spontaneous polarization, dielectric permittivity, and electrooptical properties.

Results and Discussion

Synthesis. The readily available chiral starting material for the compounds presented in this paper is (*R*)-(+)-3-methyladipic acid (Aldrich Chemie). The synthesis of the compounds was carried out according to Schemes I and II

All the compounds were synthesized using well-known procedures. In the first stages we synthesized the compounds including the "mesogenic moieties": compounds **5**, **6**, **10–12**, and **15–17**. All these processes involve reactions of etherification,[4] esterification,[4,5] and protection and deprotection of benzoic acids[6] and phenols[7] (Scheme I). Once we had obtained the intermediates, the last step in all cases consisted of the esterification of the different phenols with (*R*)-(+)-3-methyladipic acid, using *N*,*N*-dicyclohexylcarbodiimide (DCC) as an esterification agent, 4-pyrrolidinopyridine (PPY) as a catalyst, and dry tetrahydrofuran (THF) as a solvent.[8] The final products (I–

Chart I

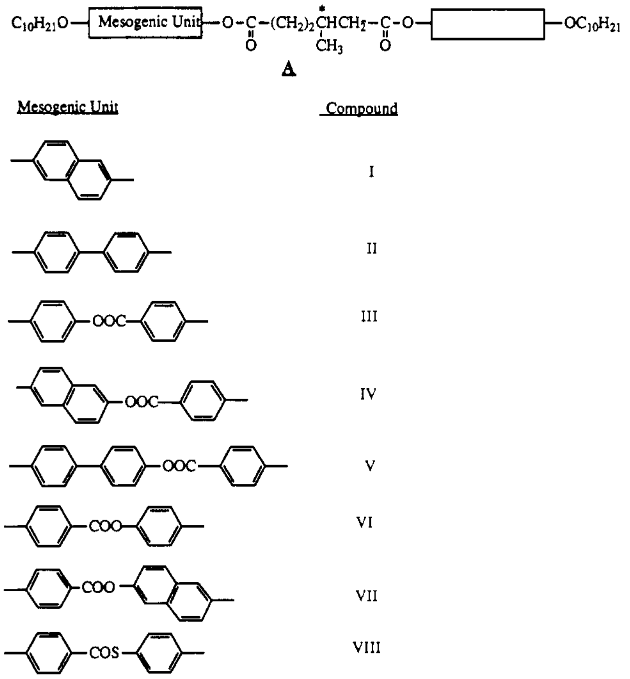

Table I. Optical, Thermal, and Thermodynamic Data[a] of the Phase Transitions[b] of Compounds I–VIII

I	C 104.2 (53.65) I
II	C 122.4 (19.85) S_1 154.2 (14.14) S_2 176.0 (40.53) I
III	C 89.2 (35.52) S_B 130.9 (7.56) S_A 180.5 (17.62) I
IV	C 120.8 (20.97) S_3 131.4 (31.93) S_C* 168.0[c] S_A 223.7 (18.85) I
V	C 142.5 (17.73) S_4 154.4 (20.83) S_5 211.5 (11.74) S_C* 240.0[c] S_A 288.7 (22.48) I
VI	C 114.3 (30.93) S_C* 135.2 (4.18) Ch 156.1 (7.01) I
VII	C 98.1 (5.55) C′ 140.0 (26.41) S_C* 167.1 (1.77) Ch 208.9 (5.07) I
VIII	C 104.2 (44.05) S_G* 126.1 (13.45) Ch 169.8 (5.89) I

[a] Data referred to the second DSC cycle. Temperature data as peak onset. [b] C, crystal; S, smectic; Ch, cholesteric; I, isotropic liquid. [c] Optical microscopy data.

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(1) Barberá, J.; Omenat, A.; Serrano, J. L. *Mol. Cryst. Liq. Cryst.* **1989**, *166*, 167.

(2) Barberá, J.; Omenat, A.; Serrano, J. L.; Sierra, T. *Liq. Cryst.* **1989**, *5*, 1775.

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(5) Twieg, R. J.; Betterton, K.; Nguyen, H. T.; Tang, W.; Hinsberg, W. *IBM Res. Rep.* RJ 6410 (62528), 8/30688.

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(8) Hassner, A.; Alexaniar, V. *Tetrahedron Lett.* **1978**, 4475.

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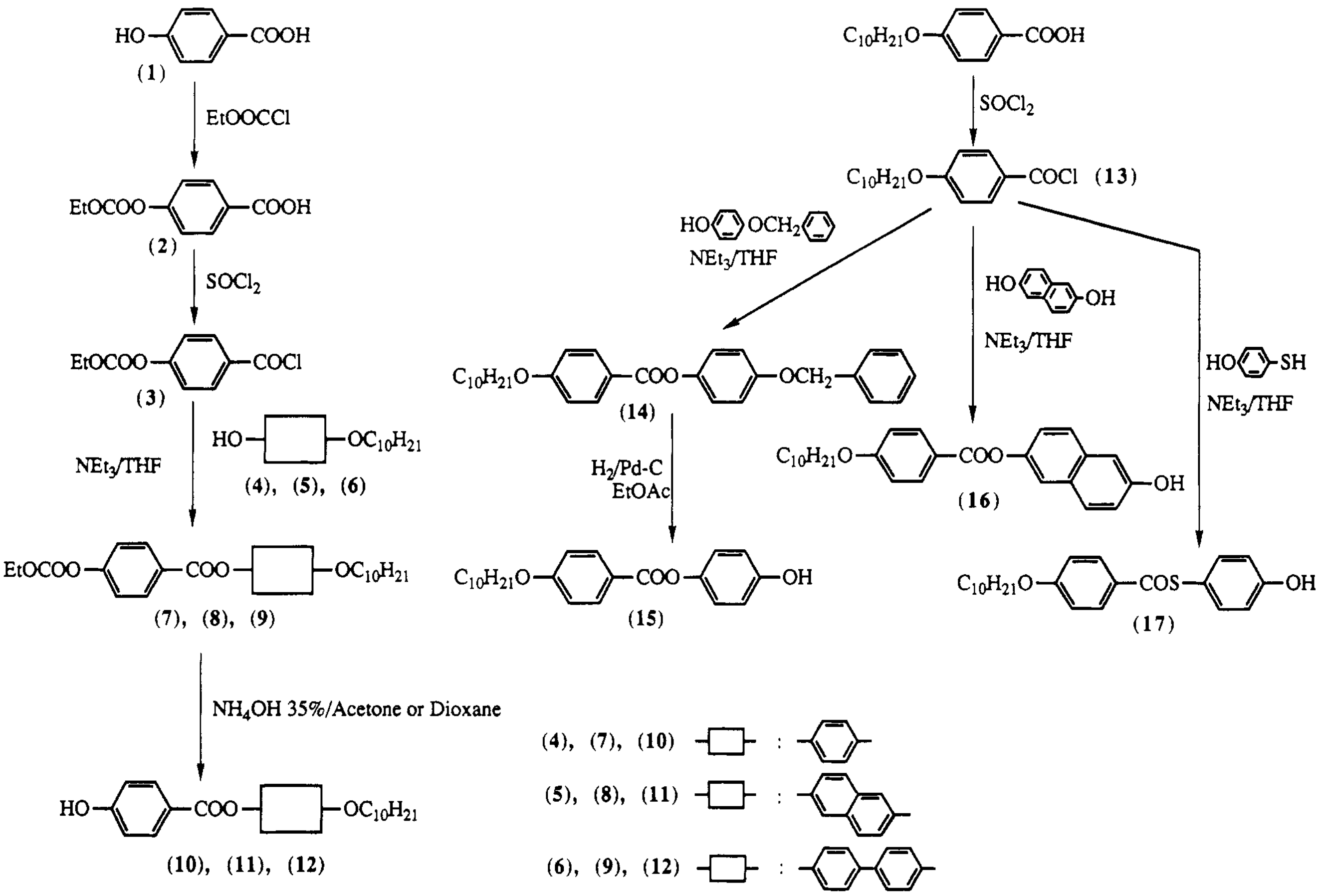
Scheme I



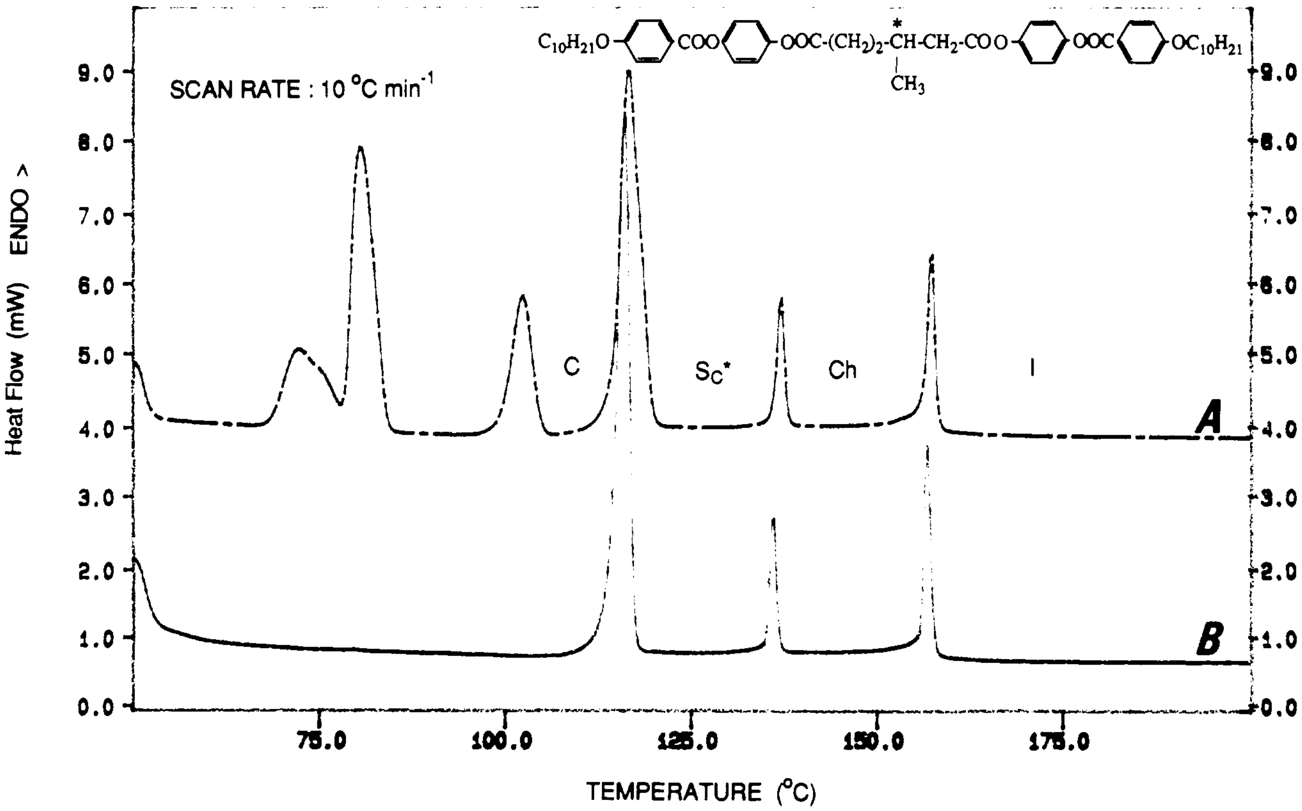


Figure 1. DSC thermograms of compound VI: (A) first heating cycle; (B) second heating cycle. Scanning rate 10 °C min^{-1}.

VIII) were purified by flash chromatography using dichloromethane as an eluent, and recrystallized from ethyl acetate several times (Scheme II).

Phase Behavior. The transition temperatures, enthalpies, and mesogenic properties for the compounds are gathered in Table I. The thermograms obtained for these compounds in the first and second heating scans are reproducible, with the exception of some crystal–crystal

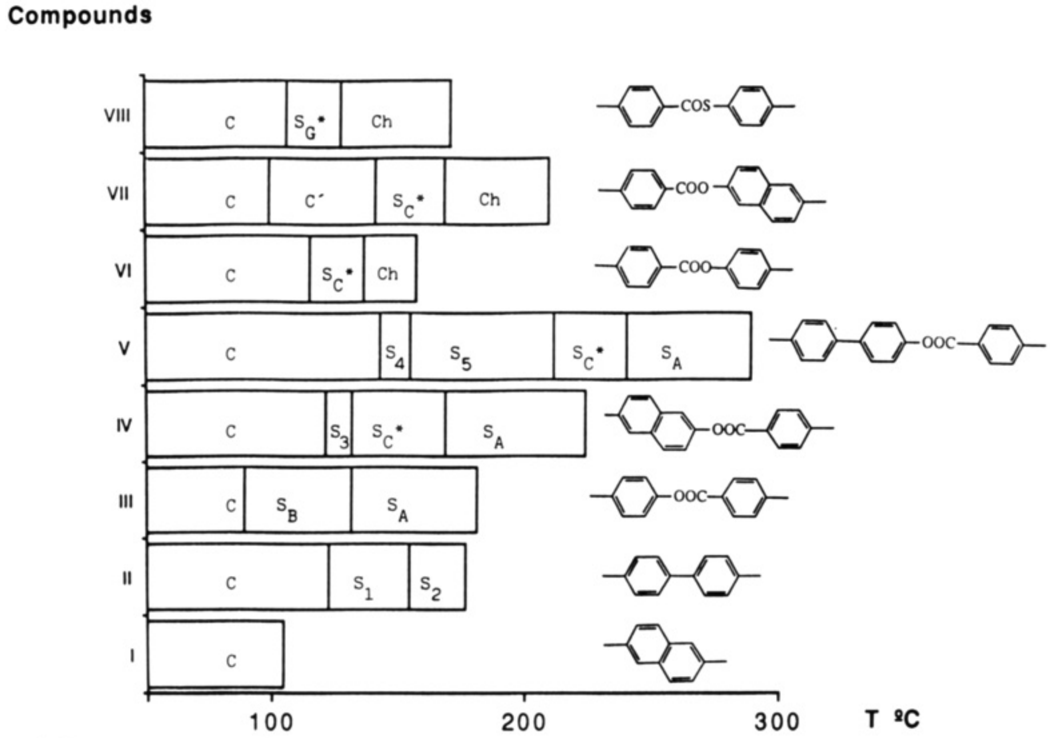


Figure 2. Phase behavior of compounds I–VIII.

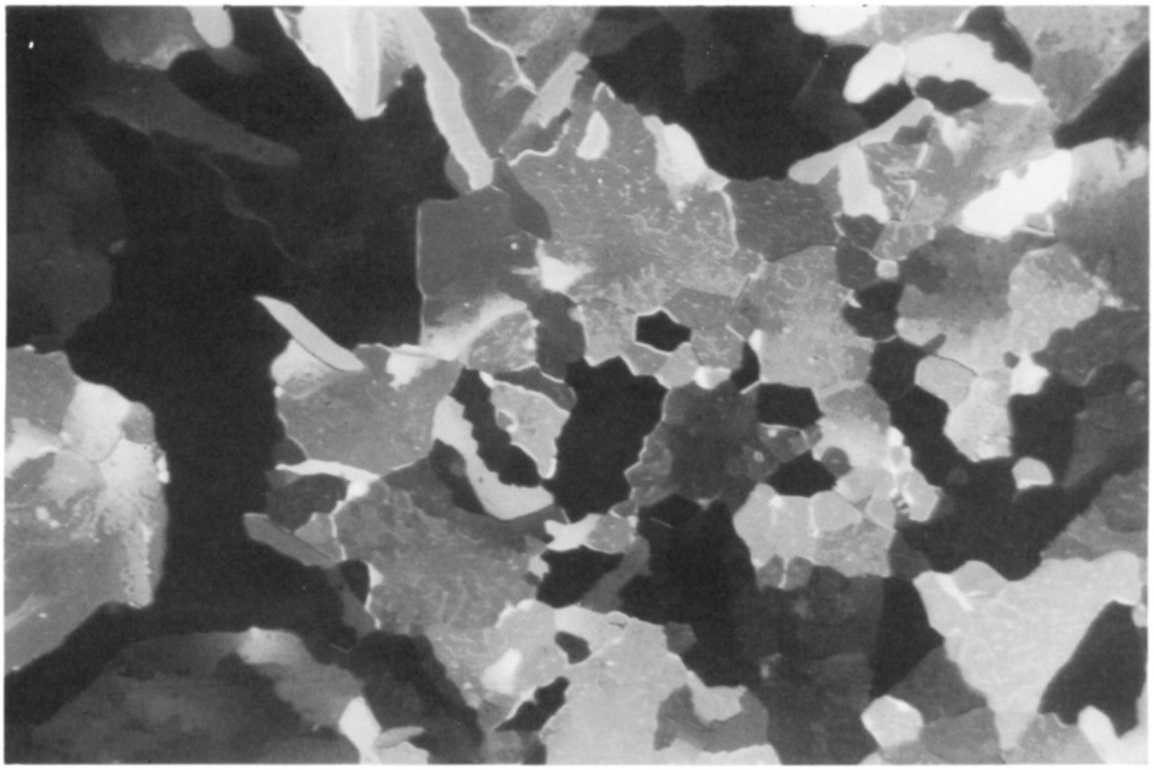


Figure 3. Photomicrograph of compound VIII at 120 °C in the G phase (magnification ×100).

transitions which appear in the first scan and disappear in the second scan (see Figure 1 as an example). The transitions and thermal data in Table I correspond to the second heating scans.

All the compounds, with the exception of I (which is not liquid crystal), show enantiotropic mesomorphic behavior (Figure 2).

The mesophases were assigned on the basis of their optical textures and in some cases confirmed by X-ray diffraction studies.

The cholesteric phase (present in compounds VI–VIII) was identified from its focal conic and oily streak textures. On cooling, the cholesteric phase transforms into a chiral smectic C* phase in compounds VI and VII, which exhibit both broken focal conic and planar textures. In the case of compound VIII, the cholesteric phase becomes a chiral smectic G phase which exhibits large sized mosaics (Figure 3). The type of phase was confirmed by X-ray diffraction measurements.

The smectic A phase present in compounds III–V ap-

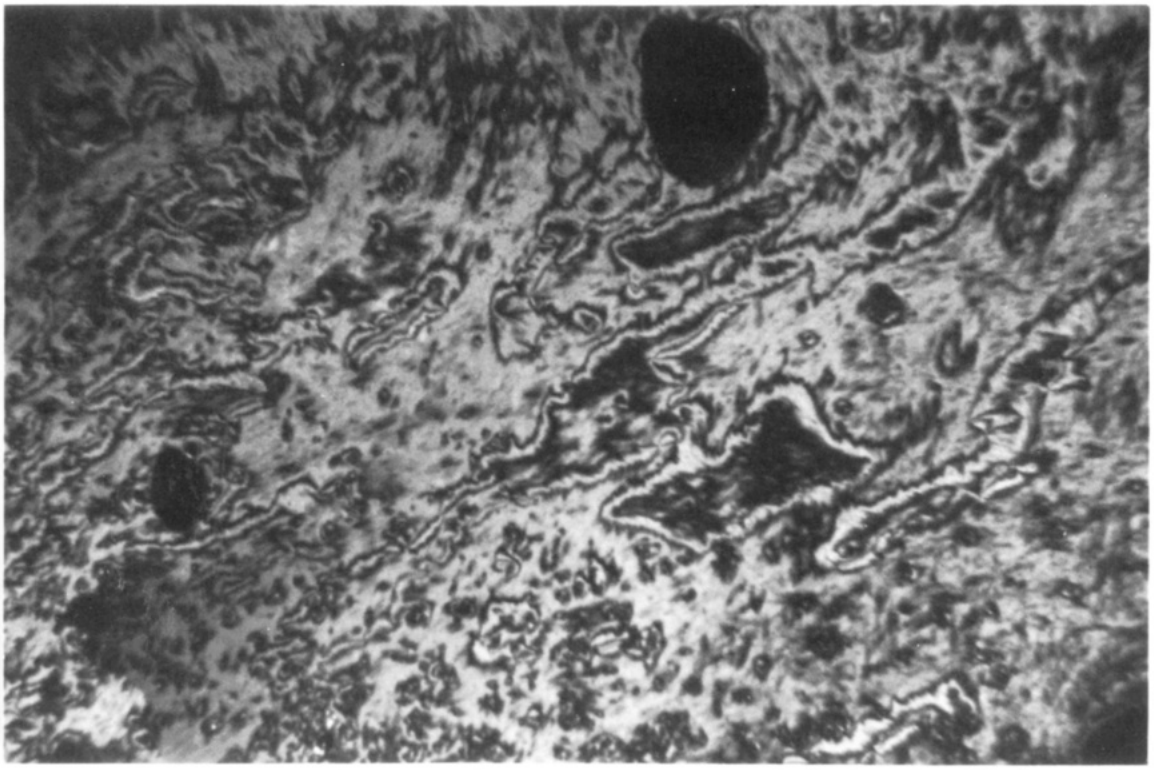
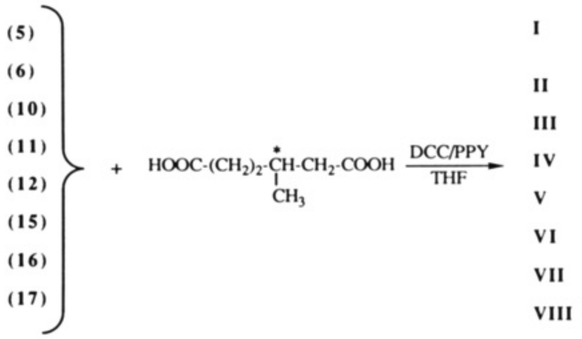


Figure 4. Photomicrograph of compound IV at 150 °C in the schlieren texture of the S_C phase (magnification ×100).

Scheme II



pears in its focal conic texture when the sample is cooled from the isotropic liquid and the phase became homeotropic when the sample was submitted to mechanical stress.

The smectic C* phase obtained on cooling the focal conic S_A phase in compounds IV and V presents the typical broken focal conic texture and if the smectic C* is formed on cooling the homeotropic smectic A texture a planar texture is observed (Figure 4)

In the case of compound III the smectic A phase transforms into a smectic B phase, which exhibits a focal conic texture but is more viscous than the smetic A.

Phases S_1, S_2, S_3, S_4, and S_5 (Table I, Figure 1) are nonfluid and could not be identified by optical observations. However, they have been classified as ordered smectic phases because they do not show supercooling effect in the DSC thermograms and appear as reversible transitions (Figure 5). The textures observed under the polarizing microscope for transitions S_1 and S_2 (from compound II) are shown in Figure 6.

Relationship between Molecular Structure and the Mesogenic Behavior. Depending on the orientation of the ester group in the mesogenic units, the compounds show different phase sequences. This has also been observed with molecules without chiral flexible spacers.[9,10] So, for compounds III and VI, which differ only in the orientation of the ester group, the appearance of orthogonal (S_A, S_B) and tilted (S_C, Ch) phases is observed. When one of the aromatic rings is naphthalene or biphenyl (compounds IV, V, and VII), a S_C* phase favored by the presence of these rings appears, although the influence of the orientation of the ester bridge is still noteworthy for the phases appearing at the highest temperatures, a cholesteric mesophase for compound VII and a smectic A mesophase for compounds IV and V. It can also be seen in Figure 2 that the presence of naphthalene and biphenyl rings greatly increases the mesogenic ranges and clearing temperatures of compounds IV and V in comparison with homologue III.

The introduction of a sulfur atom (thioester) leads to a decrease in the melting points and an increase in the clearing temperature with respect to the ester homologue (compound VI), together with a change in the mesomorphism (compound VI shows a chiral smectic C mesophase whereas compound VIII (thioester) shows a chiral smectic G phase).

Table II. X-ray Diffraction Data for Compounds III and VI–VIII

compd	phase	d_a,[a] Å	d_b,[a] Å	L,[a] Å
III	S_A	4.7	51.0	59 [illegible] 1
	S_B	4.5	55.0	
VI	S_C*	4.6	35.5	59 ± 1
VII	S_C*	4.7	39.0	64 ± 1
VIII	S_G*	4.5	37.0	60 ± 1

[a] d_a = intermolecular distance calculated applying the Bragg's law to the diagram obtained from the diffraction patterns; d_b = layer thickness calculated from the diffraction patterns; L = molecular length determined from dreiding stereomodels, considering the all trans conformation of the molecule.

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(9) Tinh, N. H.; Salleneuve, C.; Babeau, A.; Roubineaun, A.; Destrade, C. *Mol. Cryst. Liq. Cryst. Lett.* **1987**, *4*, 93.

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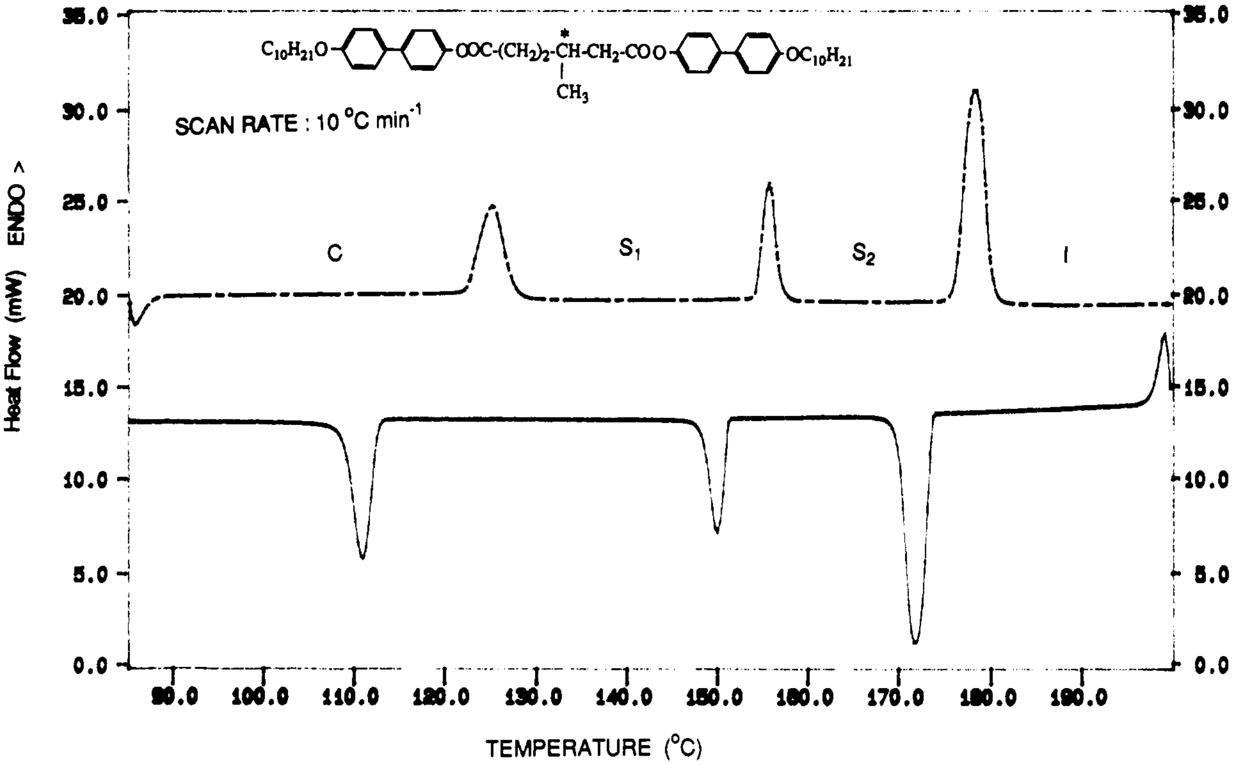

Figure 5. Heating (- - -) and cooling (—) DSC traces for compound II. Scanning rate 10 °C min^{-1}.

Some of the mesophases of these compounds were studied by X-ray diffraction using an aligning magnetic field. The results are gathered in Table II

The diffraction patterns obtained show that the only sample which is oriented in the magnetic field is that corresponding to compound III in the smectic A phase. In this case, the director of the mesophase is aligned parallel to the applied magnetic field, which means that the anisotropy of the magnetic susceptibility is positive for this compound.

From the data calculated for d_b and L it is possible to estimate the value for the tilt angle (θ) for the chiral mesophases smectic C and G of the compounds VI–VIII with the resulting values of about 50°.

The diffraction pattern obtained for compound VIII shows a pseudohexagonal arrangement of the molecules which has been attributed to a chiral smectic G phase (Figure 3).

The chiral smectic phases are not aligned by the influence of the magnetic field used in this type of measurement, as it is not strong enough to break the helical structure of the phases.

Physical Studies. In Figure 7 the dielectric permittivities of compounds VI and VIII are shown. The measurements were performed at a frequency of 105 Hz, along the direction normal to the helical structures of the chiral smectic C and chiral smectic G phases. First, a magnetic field (5000 G) was applied above the temperature of the isotropic liquid–cholesteric mesophase transition and then the sample was cooled at a rate of 10 °C/h. Once the transition had taken place, the magnetic field was removed, and the capacitance was registered during the transition from the cholesteric phase to the crystalline phase.

The dielectric response of compound VI shows the transition sequence

cholesteric 138 °C smectic C* 118 °C crystal

An increase in permittivity is observed for the smectic C phase, which is associated with the coupling of parameters related to its helical structure.

In the case of compound VIII, the dielectric response shows the following transition sequence:

cholesteric 126 °C smectic G* 103 °C crystal

A decrease in the dielectric permittivities is observed, attributed to a loss of mobility as the orientational and positional orders increased.

The Ch–S_G* transition is characterized by a sharp peak.

A phenomenologic theory has not been reported for these transitions (Ch–S_C* or Ch–S_G*), so we cannot account for this peak.

The spontaneous polarization (P_s) was measured using a method described elsewhere,[11] and no results could be obtained. We can conclude that these compounds have a very small polarization (<0.1 nC/cm^2). However, for compound VI, electrooptical switching was observed confirming the ferroelectricity of the smectic C phase. The switching response time was determined for this material using a cell 5 μm thick and applying an electric field of 150 V, 100 Hz, square wave, with a resulting value of τ = 1 ms at 130 °C. (τ was taken as the time required for a change of transmission from 10% to 90% of the difference between the two transmission levels.)

Experimental Section

Techniques. Microanalysis was performed with a Perkin-Elmer 240 B microanalyzer. Infrared spectra for all the compounds were obtained using a Perkin-Elmer 1600 (series FTIR) spectrometer in the 400–4000-cm^{-1} spectral range. ^{1}H NMR spectra were recorded on a Varian XL-200 spectrometer or a Varian Unity-300 operating at 200 or 300 MHz for ^{1}H, in deuteriochloroform or acetone-d_6 solutions. Specific rotations ($[\alpha]_D$) were measured in $CHCl_3$ at 25 °C in a Perkin-Elmer 241-C polarimeter.

The textures of the mesophases were studied with an optical microscope (Nikon) equipped with a polarizing light, a Mettler FP82 hot stage, and a Mettler central processor.

Measurements of temperatures of transition were made using

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[11] Pérez-Jubindo, M. A.; Ezcurra, A.; Etxebarría, J.; Remon, A.; Tello, M. J.; Serrano, J. L. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 137.

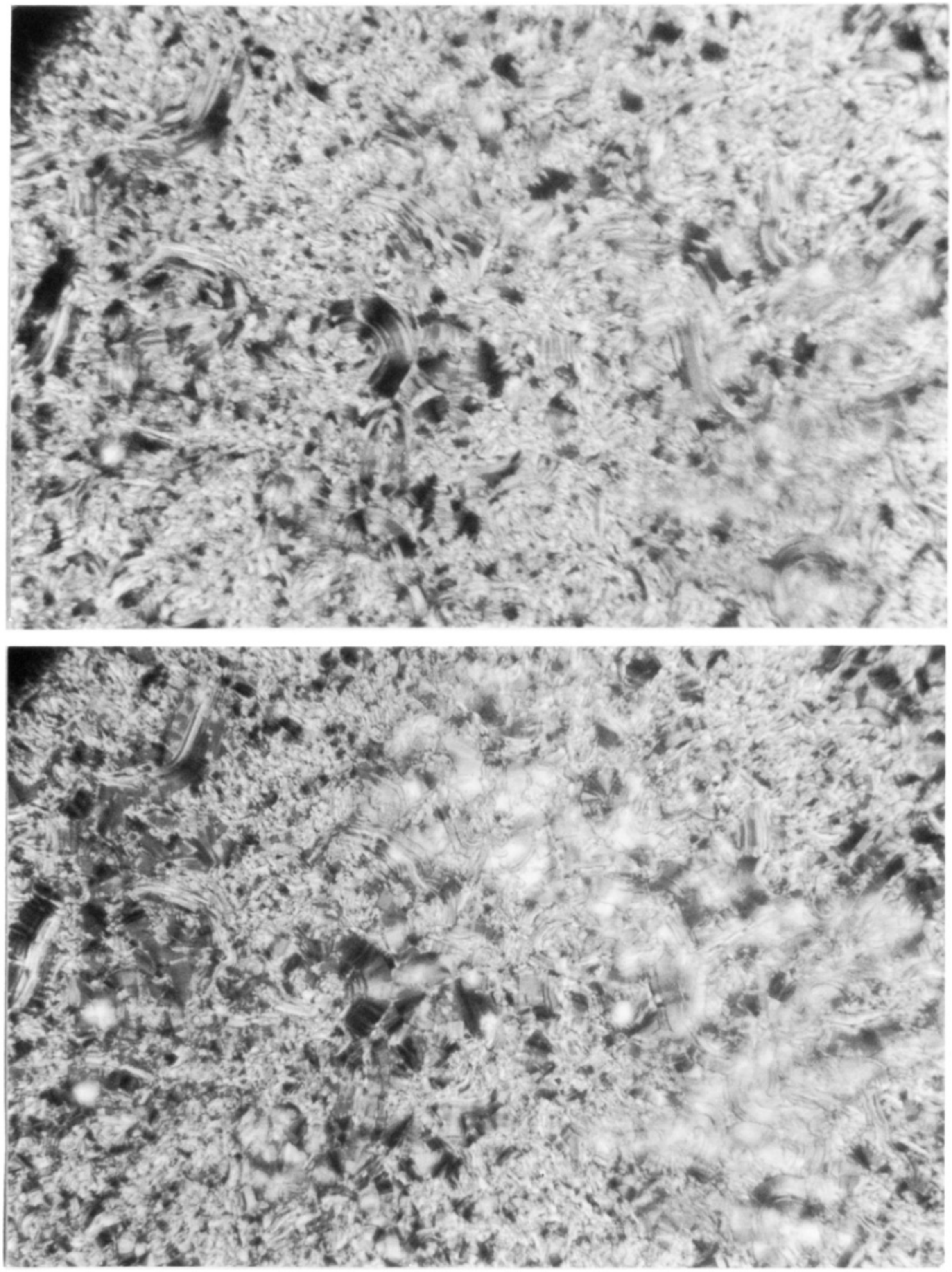

Figure 6. Photomicrographs of compound II: (a) at 146 °C in the S_1 phase; (b) at 160 °C in the S_2 phase (magnification ×100).

a Perkin-Elmer DSC-7 differential scanning calorimeter with a heating or cooling rate of 10 K/min (the apparatus was calibrated with indium (156.6 °C, 28.44 J/g) and tin (232.1 °C, 60.5 J/g)).

X-ray diffraction patterns were obtained on magnetically aligned samples. We used a point focused monochromatic Cu Kα X-ray beam issued from the reflection by a double bent pyrolytic graphite. The sample was held in a Lindemann glass tube in the inlet of a magnet (1.7 T), and the patterns were recorded on photographic film.

Dielectric measurements, switching time, and spontaneous polarization measurements were carried out in the same way described in previous papers.[11-14]

Synthesis. The general reaction pathway to the target materials (I–VIII) is shown in Schemes I and II.

The hydroxy group of 4-hydroxybenzoic acid was protected with ethyl chloroformate following a method described by Chin and

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(12) Pérez-Jubindo, M. A.; Ezcurra, A.; De la Fuente, M. R.; Santamaría, C.; Etxebarría, J.; Serrano, J. L.; Marcos, M. *Ferroelectrics* **1988**, *81*, 405.

(13) De la Fuente, M. R.; Ezcurra, A.; Pérez-Jubindo, M. A.; Zubía, J. *Liq. Cryst.* **1990**, *7*, 51.

(14) Ezcurra, A.; Pérez-Jubindo, M. A.; Etxebarría, J.; De la Fuente, M. R.; Sierra, T. *Ferroelectrics* **1989**, *92*, 325.

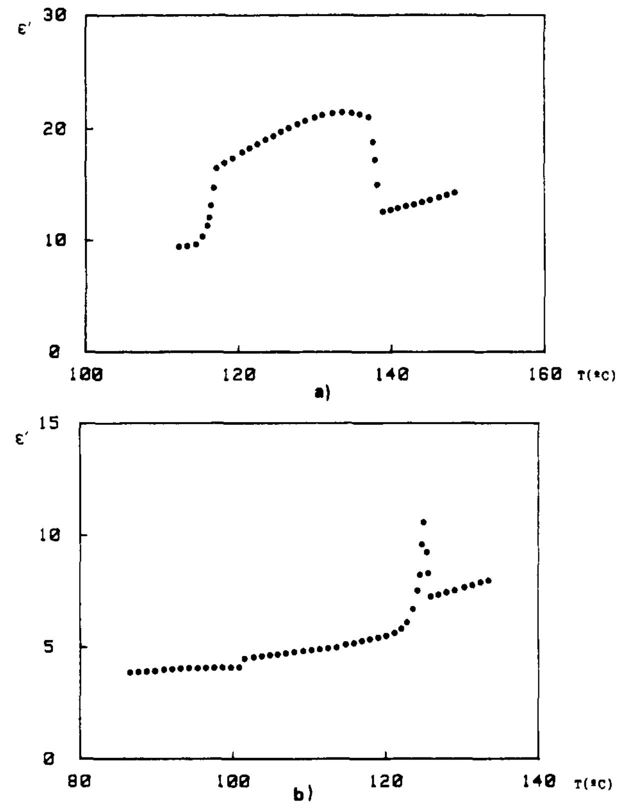

Figure 7. Temperature dependence of the dielectric permittivity of compounds (a) VI and (b) VIII at 105 Hz.

Table III. Elemental Analysis (Calculated Values in Parentheses), the Most Relevant IR Data, and Specific Rotation (in $CHCl_3$ at 25 °C)

compd	%C	%H	ν(C=O), cm^{-1}	$[\alpha]_D$, deg
I	78.2 (77.9)	8.8 (8.9)	1744	+10.3
II	79.1 (78.8)	8.9 (8.8)	1742	+11.9
III	73.7 (73.6)	8.3 (7.9)	1738	+9.7
IV	75.7 (75.9)	7.3 (7.5)	1740	-15.7
V	76.5 (76.7)	7.4 (7.5)	1739	
VI	73.9 (73.6)	8.2 (7.9)	1729	+9.0
VII	75.9 (75.9)	7.4 (7.5)	1745, 1730	+13.6
VIII	71.0 (71.0)	7.7 (7.6)	1755, 1662	+12.2

Goodby,[6] and the resulting acid (**2**) was esterified with the hydroxy derivatives **4–6** via the acid chloride[4] to give the protected species **7–9**. The protecting group was removed by reaction with aqueous ammonia 35% in acetone or THF[6] to produce the phenols **10–12**.

10: mp 144.7 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 9.32 (s, 1 H), 8.03 (dd, J_0 = 8.6 Hz, J_m = 1.0 Hz 2 H), 7.13 (dd, J_0 = 9.0 Hz, J_m = 2.4 Hz, 2 H), 6.98 (dd, J_0 = 8.6 Hz, J_m = 2.0 Hz, 2 H), 6.96 (dd, J_0 = 9.0 Hz, J_m = 2.4 Hz 2 H), 4.00 (t, 2 H), 1.85–1.57 (m, 2 H), 1.50–1.29 (m, 14 H), 0.87 (t, 3 H); IR (Nujol) 3398, 1711, 1604, 1586, 1512 cm^{-1}.

11: C 158.8 °C I (I 145.5 S_A); ^{1}H NMR (300 MHz, acetone-d_6) δ 9.36 (s, 1 H), 8.07 (d, J_0 = 8.8 Hz, 2 H), 7.83 (d, J_0 = 9.3 Hz, 1 H), 7.79 (d, J_0 = 9.3 Hz, 1 H), 7.64 (d, J_m = 2.0 Hz, 1 H), 7.33 (dd, J_0 = 8.8 Hz, J_m = 2.2 Hz 1 H), 7.31 (d, J_m = 2.2 Hz, 1 H), 7.17 (dd, J_0 = 9.0 Hz, J_m = 2.4 Hz, 1 H), 6.99 (d, J_0 = 8.8 Hz, 2 H), 4.09 (t, 2 H), 1.84–1.79 (m, 2 H), 1.52–1.26 (m, 14 H), 0.85 (t, 3 H); IR (Nujol) 3390, 1698, 1606, 1589, 1512 cm^{-1}.

12: C 204.3 °C I (I 202.8 S_A), ^{1}H NMR (300 MHz, acetone-d_6) δ 9.28 (s, 1 H), 8.03 (d, J_0 = 9.0 Hz, 2 H), 7.59 (d, J_0 = 8.6 Hz, 2 H), 7.52 (d, J_0 = 8.8 Hz, 2 H), 7.23 (d, J_0 = 8.8 Hz, 2 H), 6.95 (d, J_0 = 8.8 Hz, 2 H), 6.94 (d, J_0 = 8.8 Hz, 2 H) 3.99 (t, 2 H), 1.85–1.55 (m, 2 H), 1.33–1.25 (m, 14 H), 0.85 (t, 3 H); IR (Nujol) 3425, 1731, 1611, 1558, 1500 cm^{-1}.

The phenol intermediates **15–17** were obtained by esterification in THF/Et_3N of the 4-(benzoyloxy)phenol (which was later debenzylated to yield **15** with H_2/Pd–C following a method described in ref 7), 2,6-dihydroxynaphthalene, or 4-hydroxythiophenol with 4-(decyloxy)benzoyl chloride[4] and further purification. Com-

Table IV. ^{1}H NMR Data for Compounds I–VIII[a] (δ(ppm), Multiplicities,[b] J (Hz))

I	II	III	IV	V	VI	VII	VIII
7.71 (2 H, d, 9.0)	7.54 (4 H, d, 8.6)	8.23 (4 H, d, 8.6)	8.28 (4 H, d, 8.6)	8.25 (4 H, d, 8.6)	8.13 (4 H, d, 8.8)	8.29 (4 H, d, 8.6)	7.98 (4 H, d, 8.6)
7.76 (2 H, d, 8.8)	7.48 (2 H, d, 8.8)	7.24 (4 H, d, 8.6)	7.76 (2 H, d, 9.0)	7.59 (4 H, d, 8.8)	7.22 (4 H, d, 8.8)	7.76 (2 H, d, 9.0)	7.52 (4 H, d, 8.6)
7.48 (2 H, d, 2.2)	7.13 (4 H, d, 8.6)	7.10 (4 H, d, 8.6)	7.71 (2 H, d, 8.8)	7.50 (4 H, d, 8.8)	7.14 (4 H, d, 8.8)	7.71 (2 H, d, 9.0)	7.19 (4 H, d, 8.6)
7.21 (2 H, d, 1.8)	6.96 (4 H, d, 8.8)	6.92 (4 H, d, 8.6)	7.59 (2 H, d, 2.2)	7.26 (4 H, d, 8.6)	6.97 (4 H, d, 8.8)	7.59 (2 H, s)	6.94 (4 H, d, 8.6)
7.15 (4 H, dd, 8.8)			7.32-7.15 (10 H, m)	7.24 (4 H, d, 8.6)		7.27 (4 H, d, 8.6)	
				6.97 (4 H, d, 8.8)		7.32-7.25 (4 H, m)	
						7.18 (2 H, d, 9.0)	
4.06 (4 H, t)	3.99 (4 H, t)	3.96 (4 H, t)	4.01 (4 H, t)	4.00 (4 H, t)	4.04 (4 H, t)	4.00 (4 H, t)	4.02 (4 H, t)
2.47-2.76 (4 H, m)	2.48-2.78 (4 H, m)	2.50-2.72 (4 H, m)	2.48-2.72 (4 H, m)	2.48-2.75 (4 H, m)	2.45-2.75 (4 H, m)	2.48-2.77 (4 H, m)	2.50-2.75 (4 H, m)
2.25-2.38 (2 H, m)	2.29-2.40 (2 H, m)	2.24-2.38 (2 H, m)	2.23-2.35 (2 H, m)	2.25-2.38 (2 H, m)	2.25-2.38 (2 H, m)	2.21-2.33 (2 H, m)	2.20-2.30 (2 H, m)
2.00-2.16 (1 H, m)	2.05-2.15 (1 H, m)	2.05-2.18 (1 H, m)	1.92-2.18 (1 H, m)	2.00-2.18 (1 H, m)	2.00-2.16 (1 H, m)	1.91-2.04 (1 H, m)	2.00-2.10 (1 H, m)
1.28-1.88 (32 H, m)	1.28-1.84 (32 H, m)	1.28-1.83 (32 H, m)	1.28-1.89 (32 H, m)	1.28-1.88 (32 H, m)	1.28-1.85 (32 H, m)	1.28-1.89 (32 H, m)	1.27-1.88 (32 H, m)
1.19 (3 H, d)	1.16 (3 H, d)	1.16 (3 H, d)	1.17 (3 H, d)	1.17 (3 H, d)	1.14 (3 H, d)	1.18 (3 H, d)	1.14 (3 H, d)
0.89 (6 H, t)	0.89 (6 H, t)	0.88 (6 H, t)	0.89 (6 H, t)	0.88 (6 H, t)	0.88 (6 H, t)	0.89 (6 H, t)	0.88 (6 H, t)

[a] Spectra recorded in $CDCl_3$ at 200 MHz. [b] s, singlet; d, doublet; t, triplet; m, multiplet.

pounds 15 and 17 were recrystallized from toluene, and compound 16 was purified by flash chromatography using dichloromethane as an eluent. 4-(Decyloxy)benzoyl chloride was prepared from commercially purchased 4-(decyloxy)benzoic acid (Frinton) using thionyl chloride.[4]

15: mp 106.1 °C, ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.42 (s, 1 H), 8.08 (dd, J_0 = 9.0 Hz, J_m = 2.2 Hz, 2 H), 7.07 (dd, J_0 = 9.0 Hz, J_m = 2.2 Hz, 2 H), 7.05 (dd, J_0 = 9.0 Hz, J_m = 2.4 Hz, 2 H), 6.87 (dd, J_0 = 9.0 Hz, J_m = 2.4 Hz, 2 H), 4.11 (t, 2 H), 1.83–1.49 (m, 2 H), 1.34–1.29 (m, 14 H), 0.87 (t, 3 H); IR (Nujol) 3463, 1709, 1605, 1511, 1469 cm^{-1}.

16: C 136.0 °C N 148.5 I; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.2 (d, J_0 = 9 Hz, 2 H), 7.61 (d, J_0 = 8.3 Hz, 1 H), 7.6 (d, J_0 = 8.6 Hz, 1 H), 7.55 (d, J_m = 2.1 Hz, 1 H), 7.25 (dd, J_0 = 8.5 Hz, J_m = 1.5 Hz, 1 H), 7.06–7.02 (m 2 H), 6.99 (d, J_0 = 9 Hz, 2 H), 6.04 (s, 1 H), 4.05 (t, 2 H), 1.85–1.81 (m, 2 H), 1.48–1.28 (m, 14 H), 0.89 (t, 3 H); IR (Nujol) 3382, 1706, 1605, 1510, 1462, 1260 cm^{-1}.

17: C 130.8 °C I (I 111.8 N), lit.[5] C 130.5–131.3 °C (N)*; ^{1}H NMR (200 MHz $CDCl_3$) δ 7.98 (d, J_0 = 9.0 Hz, 2 H), 7.30 (d, J_0 = 9.0 Hz, 2 H), 6.90 (d, J_0 = 9.0 Hz, 2 H), 6.74 (d, J_0 = 9.0 Hz, 2 H), 4.00 (t, 2 H), 2.41 (s, 1 H), 1.95–1.55 (m, 2 H), 1.25 (m, 14 H), 0.85 (t, 3 H); IR (Nujol) 3377, 1643, 1597, 1507, 1494 cm^{-1}.

The compounds 4–6 were prepared using a standard procedure[4] from the corresponding hydroxy compound and decyl bromide in KOH/EtOH.

The phenols 5, 6, 10–12, and 15–17 were finally coupled with (*R*)-(+)-3-methyladipic acid using *N*,*N*-dicyclohexylcarbodiimide (DCC) as an esterification agent, 4-pyrrolidinopyridine (PPY) as a catalyst, and dried tetrahydrofuran (THF) as a solvent following a method described in the literature.[8] The corresponding elemental analysis, the most relevant IR data, and the $[\alpha]_D$ values are given in Table III. The ^{1}H NMR data for I–VIII are gathered in Table IV.

Conclusions

This new type of liquid crystal incorporating the chiral center in a flexible spacer between two identical mesogenic units shows ferroelectric behavior, although the values for P_s seem to be small. We were able to measure a response time of 1 ms for one of these compounds. Taking into account the data obtained for these compounds, we are working on the synthesis of new dimers with different flexible spacers which will hopefully have better ferroelectric properties. The results will be reported elsewhere.

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Synthesis of Cadmium Sulfide in Situ in Reverse Micelles: Influence of the Preparation Modes on Size, Polydispersity, and Photochemical Reactions

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We present results obtained by using reverse micelles of either sodium bis(2-ethylhexyl)sulfosuccinate (AOT) or mixed cadmium and sodium bis(2-ethylhexyl)sulfosuccinate ($AOT/Cd(AOT)_2$) to form CdS semiconductor particles. The control of size, polydispersity, and the photochemical reactions are compared by using various mode of synthesis of CdS. Three different reverse micellar systems have been used: the cadmium ions are solubilized in AOT reverse micelles either in the presence or in the absence of a protecting polymer such as HMP ($Cd(NO_3)_2$/±HMP/AOT/isooctane/water reverse micelles} or associated with bis(2-ethylhexyl)sulfosuccinate ($Cd(AOT)_2$/AOT/isooctane/water) reverse micelles. The size of the CdS particles is found to increase with the water content. The polydispersity strongly depends on the mode of CdS synthesis. At low water content, reverse micelles protect CdS semiconductors from photocorrosion. At higher water content, photocorrosion process depends on the x value, on the presence of HMP, and on the participation mode of cadmium ions ($Cd(NO_3)_2$ and $Cd(AOT)_2$) in the synthesis. The photoelectron-transfer reactions from CdS particles to different dialkyl viologens have been studied. The variation in the yield strongly depends on the relative value of the cadmium over sulfide ions concentrations and on the presence of sulfide clusters bound to the CdS at interface. It is possible to gelify the reverse micellar system and form semiconductors in isotropic gel using the various systems described previously.

Introduction

The use of dispersed media to solubilize or synthesise microparticles in situ has made considerable progress in the last few years: Langmuir-Blodget films,[1] vesicles,[2] polymerized vesicles,[3] double layers,[4] inert polymeric matrix,[5] or reverse micelles[6-15] have been used as the in-

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