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Liquid Crystals

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M. Marcos^a; A. Omenat^a; J. L. Serrano^a

^a Departamento de Química Orgánica, Institute de Ciencia de Materiales de Aragón, Zaragoza, Spain

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Novel ferroelectric non-symmetric dimeric liquid crystals

by M. MARCOS, A. OMENAT and J. L. SERRANO*

Departamento de Química Orgánica,
Instituto de Ciencia de Materiales de Aragón,
Facultad de Ciencias, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

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The synthesis, characterization, mesomorphism and ferroelectric behaviour of ten new chiral dimeric compounds are reported. These compounds are non-symmetric dimers consisting of two mesogenic units joined by two different flexible spacers derived from *S*(-)-lactic acid. The mesogenic units contain ester and thioester groups. The effects of the length of the flexible spacer and the structure of the mesogenic units on the mesomorphism of the compounds are investigated. These compounds are ferroelectric and the spontaneous polarizations of some were measured, giving values of *c.* 10 nC cm⁻².

1. Introduction

Since the discovery of the first ferroelectric liquid crystal in 1975 by Meyer *et al.* [1], thousands of compounds which display ferroelectric behaviour have been synthesized. Most of them consist of a mesogenic central core and two terminal chains, one of which supports an asymmetric carbon.

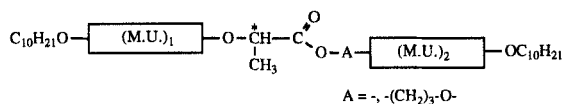
In recent years, attempts have been made to obtain ferroelectric liquid crystals with new and different structures. The differences in these new structures reside in the position of the chiral centre in the molecule: it may be located in the mesogenic core, for example, in a chiral heterocycle [2], or in a flexible spacer which joins two mesogenic units [3, 4]. We have been also working on this second new type of structure and have reported the mesomorphic and ferroelectric behaviour of different series of dimeric compounds which incorporate a chiral centre in a flexible spacer [5-7].

In order to improve the ferroelectric properties of this type of compound and as a continuation of this work, we have synthesized and studied ten new compounds consisting of two mesogenic units with ester and thioester linkage groups, joined by two different flexible spacers derived from *S*(-)-lactic acid (see figure 1).

It is noteworthy that these compounds are non-symmetric dimers, as the two mesogenic units in a compound are different, thus avoiding the cancellation of partial dipole moments in the molecule. Additionally, the chiral centre is close to one of the mesogenic units and surrounded by strong dipole moments (ether and ester). All these factors might favour the generation of a significant spontaneous polarization in these materials.

The mesomorphic behaviour of these compounds was studied by means of optical microscopy and differential scanning calorimetry, and physical studies were carried out in order to determine spontaneous polarizations and response times.

* Author for correspondence.



Compound	(M.U.) ₁	(M.U.) ₂	A
I			—
II			—
III			—
IV			-(CH ₂) ₃ -O-
V			-(CH ₂) ₃ -O-
VI			-(CH ₂) ₃ -O-
VII			-(CH ₂) ₃ -O-
VIII			-(CH ₂) ₃ -O-
IX			-(CH ₂) ₃ -O-
X			-(CH ₂) ₃ -O-

Figure 1. Chiral dimers synthesized.

2. Experimental

2.1. Synthesis

The synthesis of the dimeric compounds was carried out as shown in figure 2. The preparation of *S*(-)-benzyl lactate (**1**) was performed as described by Chan *et al.* [8]. This intermediate was condensed with the phenols **2** using diethyl azodicarboxylate (DEAD) and triphenylphosphine [9, 10]. The synthesis of the phenols **2** is described elsewhere [7]. The next step involved deprotection of the acid group by hydrogenation of the compounds **3** [11].

The second part of the scheme deals with the preparation of the intermediates **6** involved in the synthesis of the final dimers IV–X. It consists of the condensation of the phenols **5** with propan-1,3-diol using the aforementioned etherification method (DEAD/Ph₃P). The synthesis of the phenols **5** is described elsewhere [7].

The last step is the esterification reaction using dicyclohexylcarbodiimide (DCC), in tetrahydrofuran (THF) with 4-pyrrolidinopyridine (PPY) as a catalyst, to yield the final dimers I–X [12].

Previous experience using this method gave evidence for a partial racemization of the asymmetric centres when the substrate was an α -halo-acid [13]. Thus, before choosing this method, we carried out ¹H-NMR studies to make sure that our substrate did not undergo racemization.

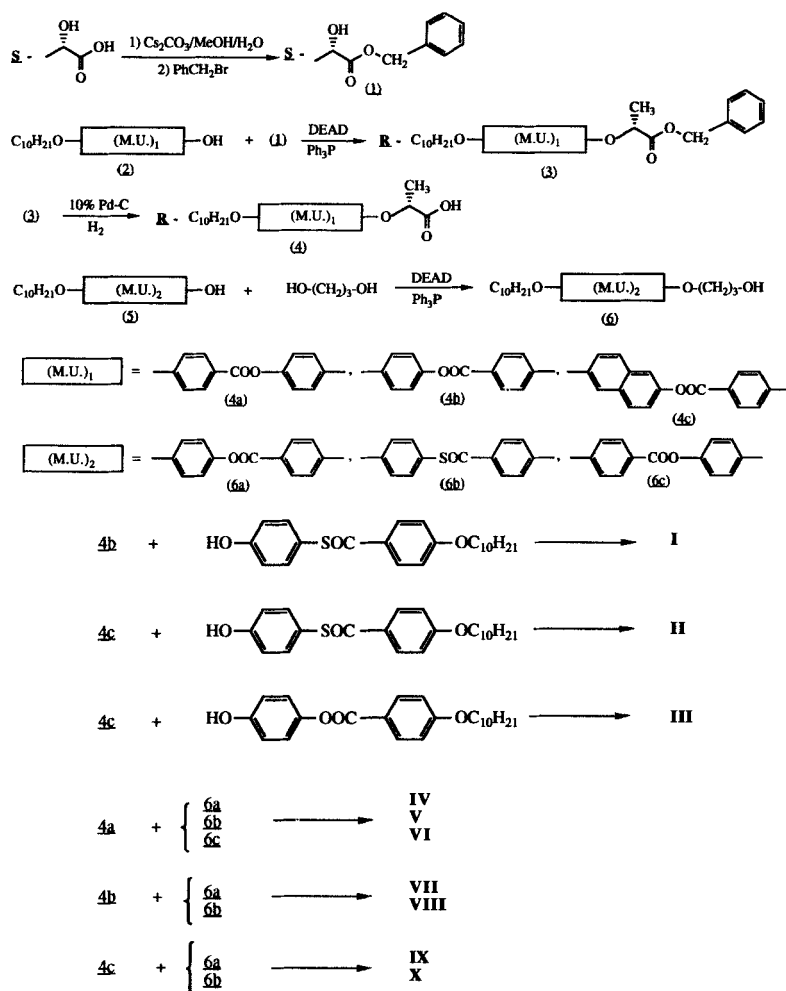


Figure 2. Synthetic route for compounds I–X.

We synthesized compounds A and B, as shown in figure 3. The presence of a second asymmetric centre would give rise to two diastereoisomers if racemization occurs. Thus, we also studied this possibility by ^1H NMR. The results obtained proved that esterification using DCC does not produce partial or total racemization of the chiral centre involved in the reaction, as only one diastereoisomer is detected.

2.2. Techniques

Infrared spectra for all the compounds were obtained using a Perkin–Elmer 1600 (Series FTIR) spectrometer in the $400\text{--}4000\text{ cm}^{-1}$ spectral range. ^1H NMR spectra were recorded using a Varian XL-200 spectrometer or a Varian Unity-300 operating at 200 or 300 MHz for ^1H and solutions in deuteriochloroform. Elemental analyses were performed using a Perkin–Elmer 248B microanalyser.

The textures of the mesophases were studied by polarizing optical microscopy (Nikon) combined with a Mettler FP 82 hot stage, and a Mettler central processor.

Measurements of temperatures of transition were made using a Perkin–Elmer DSC-7 differential scanning calorimeter with a heating or cooling rate of $10^\circ\text{C min}^{-1}$

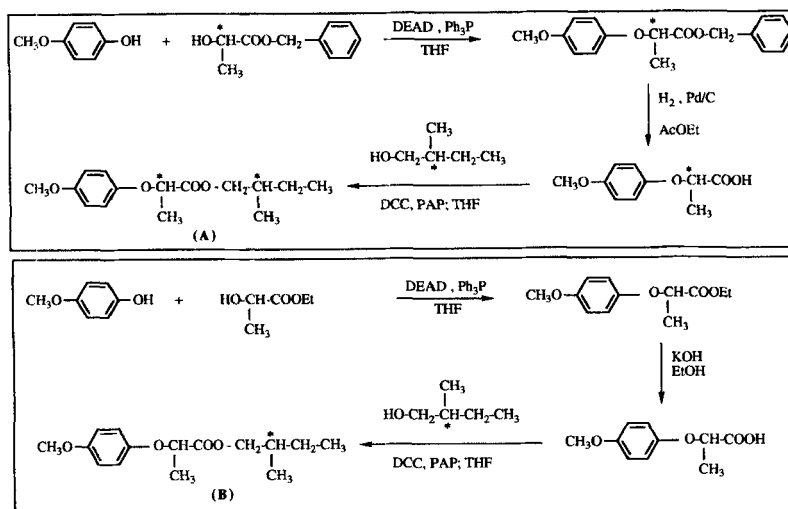


Figure 3. Synthetic route for compounds A and B.

(the apparatus was calibrated with indium (156.6°C , 28.44 J g^{-1}) and tin (232.1°C , 60.5 J g^{-1})). Dielectric and spontaneous polarization measurements were carried out as described in previous papers [14–17].

3. Results and discussion

3.1. Mesomorphic behaviour

The optical and thermal data for compounds I–X are gathered in the table.

With regard to the first three compounds (I–III) with a very short flexible spacer, only compound II was mesomorphic, showing a monotropic chiral smectic C phase. As we observed in our previous work [7], the thioester linkage in a mesogenic unit produced a decrease in the melting temperature with respect to the carboxylic ester (*c.* 20°C —compounds II and III), and the presence of naphthalene rings favours S_{C}^* mesomorphism. These two facts may explain the monotropic S_{C}^* behaviour of compound II. The lengthening of the flexible spacer (compounds IV–X) gave rise to monotropic mesomorphism in all seven cases.

This behaviour is similar to that observed for dimers formed using two mesogenic units joined by a non-branched flexible spacer [18–20]. In many cases, it has been found that the smectic behaviour shown by the monomer is lost for the dimeric compound [19]. However, some examples of smectic materials have been reported [20]. These compounds show nematic and/or smectic phases depending on the lengths of their terminal chains and flexible spacer. The mesomorphism shown by dimers with a flexible spacer formed by 6–10 atoms is much richer than that exhibited by compounds with shorter or longer spacers.

We have also observed that a ramification (chiral centre) introduced in the centre of the flexible spacer does not prevent the appearance of enantiotropic cholesteric and smectic phases [4, 7]. For dimers I–X, however, the chiral centre is located very close to one of the mesogenic units, making the orientation of the molecules in a mesophase difficult. This prevents the existence of stable enantiotropic mesophases.

It has not been possible to find any clear relationship between the nature of the mesogenic unit and the mesomorphism shown by the materials, as was the case for

Optical, thermal and thermodynamic data for compounds I-X†.

Compound	Transition	Temperature/°C	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/R$
I	C-I	115.7	48.1	14.9
II	C-I	137.1	46.7	13.7
	I-S _C ‡	134.4	16.0	4.7
III	C-I	156.3	64.5	18.1
IV	C-I	105.9	71.3	22.6
	I-S‡	74.2		
V	C-I	97.6	82.4	26.7
	I-Ch‡	83.7	2.4	0.8
	Ch-S _A ‡	81.6	4.7	1.6
VI	C-I	97.1	81.8	26.6
	I-S _C ‡	86.6	11.5	3.8
VII	C-I	98.2	66.2	21.5
	I-Ch‡	78.5		
	Ch-S _C ‡	77.1	9.4§	
VIII	C-I	104.9	74.2	23.6
	I-Ch‡	83.7		
	Ch-S _A ‡	80.4	7.9§	
IX	C-I	103.8	56.7	18.1
	I-Ch‡	101.3	3.4	1.1
	Ch-S _C ‡	93.5	1.9	0.6
X	C-I	115.5	66.8	20.7
	I-Ch‡	108.4	3.1	1.0
	Ch-S _C ‡	99.7	1.5	0.5

† Tables of IR, microanalytical and ¹H NMR data for compounds I-X and ¹H NMR data for compounds A and B have been deposited with the British Library. Copies of these tables which comprise 4 pages may be obtained from the British Library, Lending Division, by quoting the number SUP 16523 according to the procedure described at the end of this issue.

‡ Monotropic transition.

§ No resolved transitions. This value corresponds to the combined enthalpies.

other dimers incorporating the *R*(+)-3-methyladipoyl moiety as a flexible spacer [7]. We can only point out that a naphthalene ring in one of the mesogenic units IX and X does favour S_C* mesomorphism. The behaviour of the rest of the compounds (IV-VIII) with benzene rings in the mesogenic units depends on the type of linkage: ester groups give rise to S_C* mesomorphism and compounds with thioester groups show S_A behaviour. However, the orientation of the ester group does not appear to have a clear influence on the type of mesomorphism shown by the materials.

Mesophases were identified by observation of their textures by optical microscopy [21, 22]. Cholesteric phases were clearly identified by their focal-conic and oily-streak textures. Chiral smectic C phases, formed from cholesteric phases, retained a similar texture: platelet or homogeneous texture for a phase formed from an oily-streak texture, and focal-conic texture from the analogous cholesteric focal-conic texture. Smectic A phases showed the typical focal-conic texture which became homeotropic on applying mechanical stress to the sample. Mesophase S (compound IV) could not be identified clearly by optical microscopy; it is a very viscous tilted smectic phase.

3.2. *Ferroelectric properties*

Five of the compounds show a monotropic S_C^* phase, potentially ferroelectric. The spontaneous polarization and the switching time were obtained simultaneously by using the triangular wave method [16, 23, 24] with an electric field of $3.3 \times 10^3 \text{ KV}_{pp/m}$ and 50 Hz.

Figure 4 shows the temperature dependence of the spontaneous polarization for compounds VI and IX respectively.

The results obtained for the $P_{s, \max}$ and switching characteristics are the following:

Compound	$P_{s, \max}/\text{nC cm}^{-2}$	$\tau E/\mu\text{sV } \mu\text{m}^{-1}$
VI	8.5	340
IX	6.9	680

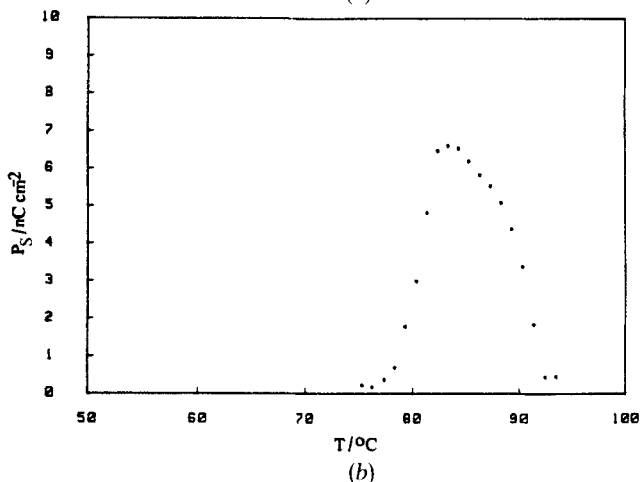
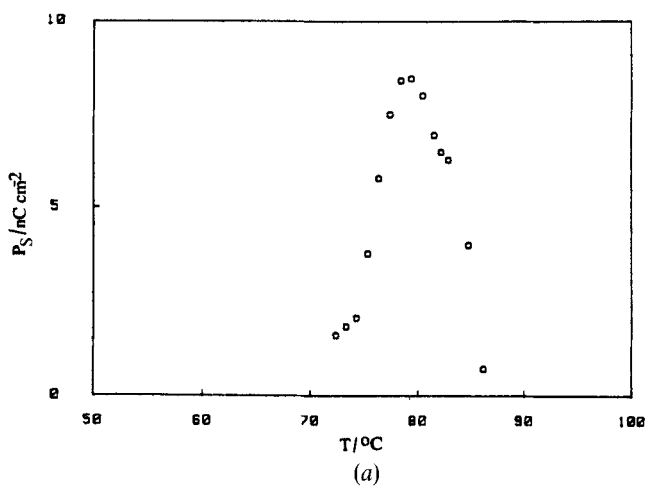


Figure 4. (a) Temperature dependence of the spontaneous polarization of compound VI. (b) Temperature dependence of the spontaneous polarization of compound IX.

The response times present reasonably high values which can be related to the relatively small values for spontaneous polarization. It was not possible to measure the P_s values for the rest of the compounds, due to the monotropic character of their S_C^* phases and the ready onset of crystallization.

When some of these materials were studied, measurement of the dielectric constant as a function of the temperature did not show a clear transition to the S_C^* phase. We must conclude that in these cases, the S_C^* phase is hardly developed before it disappears. In these conditions, it is not possible to detect spontaneous polarization.

The physical studies of the non- S_C^* materials were carried out using their mixtures with a non-chiral smectic C compound. The mixtures consisted of 10 per cent of the chiral compound and 90 per cent of 4-decyloxyphenyl 4-hexyloxybenzoate. The electro-optical behaviour of these mixtures proved their ferroelectric nature, as we could observe typical switching of the samples under the action of electric fields. It was not, however, possible to measure their spontaneous polarizations due to the low values resulting from mixtures containing only 10 per cent of the chiral component, although for the mixture containing compound VIII, a polarization of less than 1 nC cm^{-2} was indicated; as already noted, it was not possible to determine an accurate value for the pure compound.

4. Conclusions

Compounds I, II and III, with the *R*-2-oxypropanoyloxy moiety as a spacer (4 atoms), show poor mesogenic properties. However, when the spacer is extended to 8 atoms by means of the 1,3-propanedioxy group (compounds IV–X), the materials show monotropic mesomorphism (Ch, S_A , S_C^*).

Physical measurements were carried out in order to establish the ferroelectric nature of this type of dimer. Low P_s values could be determined for two of these compounds. We can conclude that the introduction of the chiral centre into a flexible spacer between two mesogenic units gives rise to ferroelectric materials with low values of P_s .

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