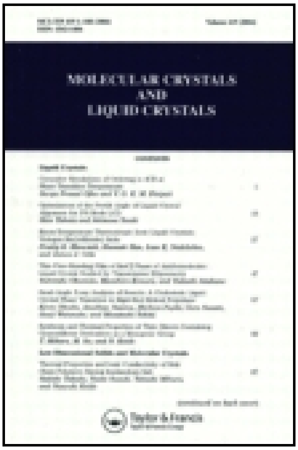

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New Chiral Smectic Liquid Crystals with The Assymetrical Carbon in The Central Part of The Molecule

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New Chiral Smectic Liquid Crystals with The Assymetrical Carbon in The Central Part of The Molecule

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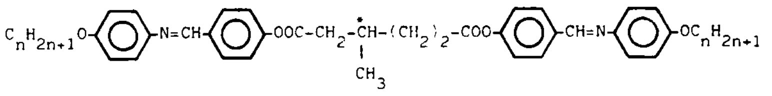
A new family of mesogenic compounds has been synthesized. The series consists of seven chiral dimers with the chiral center in the central flexible spacer of the dimeric structure. All of the materials are mesomorphic. Most of them exhibit tilted smectic phases and consequently could be of interest as the first ferroelectric liquid crystals with the chiral center in the central core of the molecule.

INTRODUCTION

Many mesomorphic compounds have been reported in the literature with a chiral center in one of the terminal groups, but until recently no liquid crystalline compounds with the chiral center in the central core part of the molecule had been described. In the field of polymer liquid crystals, chiral moieties have however been used as flexible spacers, giving rise to cholesteric properties.[1]

As an application of this concept to low molecular weight compounds, we have synthesized and studied the mesomorphic properties of a new series of dimeric compounds with a chiral flexible spacer in their structure. This has already been put into practice for other purposes, but in most cases no mesomorphic compounds have been obtained.[2]

The compounds described in this paper are *bis*-azomethines containing the R-3-methyladipoyl group as a central flexible spacer; the general formula is as follows:



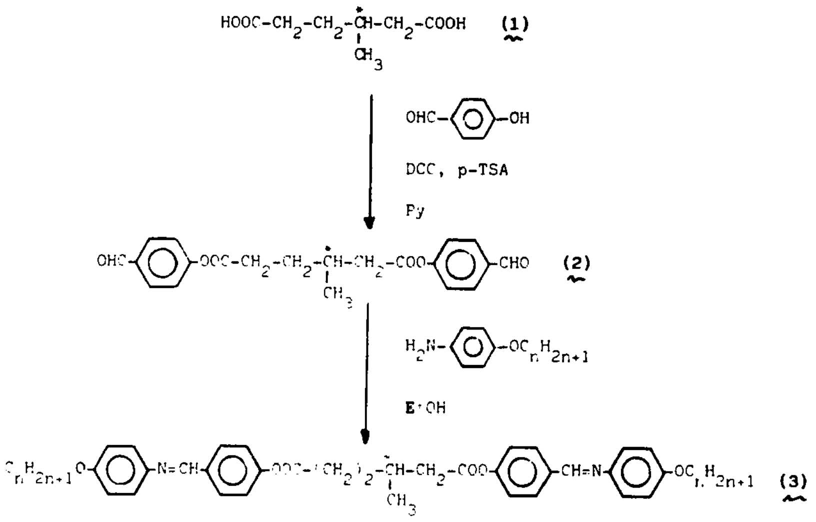
n = 2,4,6,8,10,12,14.

We have studied the mesomorphic behavior of these compounds by optical microscopy and differential scanning calorimetry.

EXPERIMENTAL

Synthesis

The compounds described in this paper were prepared as shown in the following synthetic scheme:



Bis-(4′-formylphenyl) R-3-methyladipate (**2**) was obtained by esterification of R-3-methyladipic acid (**1**) with 4-hydroxybenzaldehyde using the procedure of Chen and Jones.[3]

A solution of R-3-methyladipic acid (1.0 g, 0.0062 mol) 4-hydroxybenzaldehyde (1.53 g, 0.0124 mol), dicyclohexylcarbodiimide (DCC) (2.68 g, 0.013 mol), and *p*-toluenesulfonic acid (0.14 g) in pyridine (45 ml) was stirred at 25°C. A white solid began to precipitate. After stirring for 18 h, the solid was removed by filtration. The mixture was concentrated by rotary evaporation, and the residue dissolved in CH_2Cl_2, and washed with 10% HCl and water. The solution was filtered and concentrated. The solid residue was washed repeatedly with distilled water until the water was neutral, crystallized from aqueous ethanol, and dried to give 700 mg (30%) of (**2**).

The final products (**3**) were prepared by condensation of (**2**) with the appropriate 4-alkoxyaniline following the method of Keller and Liebert.[4]

A solution of 0.5 mmol of (**2**) and the appropriate 4-alkoxyaniline (1 mmol) in ethanol (5 ml) was stirred at room temperature for 2 h. The solid obtained was filtered and crystallized from an appropriate solvent (see Table I).

Techniques

The melting points, transition temperatures and enthalpies were determined using a PERKIN-ELMER DSC-2 Differential Scanning Calorimeter. The heating rate

TABLE I

Solvents for crystallization and yields

n	Solvent	Yield (%)
2	Ethanol	45
4	Acetone	49
6	Acetone	42
8	Acetone	44
10	Ethyl acetate	45
12	Ethyl acetate	65
14	Ethyl acetate	43

was 10 K/min. The apparatus was calibrated by measuring the known melting point and heat of fusion of indium (429.6 K, 6.8 cal/g)

The optical observations were made using a REICHTER-THERMOVAR HT-1 B11 Polarizing Microscope equipped with a heating stage.

The identification of products was carried out by the usual spectroscopic methods: UV (PERKIN-ELMER 200), IR (PERKIN-ELMER 283), NMR (BRUKER WP-80-SY).

The purity of all products was checked by the aforementioned techniques, by elemental analysis (C, H, N), and by thin-layer chromatography.

RESULTS AND DISCUSSION

The transition temperatures, enthalpies, and mesomorphic properties of the series are gathered in Table II.

The variation in the mesomorphic behavior as a function of length of the terminal alkoxyl chain is shown in Figure 1.

Chiral (cholesteric or tilted smectic) mesophases occur for all the compounds. A cholesteric mesophase was observed only for the compounds with short terminal chains ($n \leq 6$). From $n = 4$ onwards, smectic phases appear. The miscroscopic textures and D.S.C. results suggest that S_1 and S_2 are S_H and S_G phases respectively. Both are non-fluid phases, and the S_2 phase gives a sharp and large D.S.C. peak at the transition to higher temperature mesophases. The wide temperature ranges for the S_2 mesophase in most of the compounds (see Figure 1) are noteworthy.

A S_A phase appears in compounds with $n = 6, 8, 10$, but in the case of $n = 10$, the thermal range is small (about 5°C), much narrower than for the first two compounds. The existence of a S_C^* phase in compounds with $n = 10, 12, 14$ is important because of its potential ferroelectric nature. It is also noticeable that from $n = 10$, one of the ordered smectic phases, S_1, disappears and at the same time a S_C^* mesophase appears.

TABLE II

Transition temperatures, enthalpies and derived entropies for the compounds in the series

n	Transition	*T*(°C)	ΔH(kcal/mol)	ΔS(cal/mol K)
2	C—Ch	156.3	8.7	20.3
	Ch—I	236.6	1.8	3.5
4	C—S_1	154.6	10.0	—
	S_1—S_2[a]	158.5		
	S_2—Ch	169.3		
	Ch—I	210.9	1.4	2.9
6	C—S_1	122.8	3.2	8.1
	S_1—S_2	140.0	0.6	1.4
	S_2—S_A	174.7	4.6	10.2
	S_A—Ch	190.0	2.8	—
	Ch—I	195.5		
8	C—S_1	121.3	3.7	9.4
	S_1—S_2	130.8	1.0	2.4
	S_2—S_A	171.2	3.7	8.3
	S_A—I	190.0	4.3	9.1
10	C—S_1	122.1	7.5	—
	S_1—S_2	122.4		
	S_2—S_C^*	167.4	3.2	7.3
	S_C^*—S_A[b]	190	—	—
	S_A—I	194.4	4.6	9.8
12	C—S_2	121.8	11.3	28.5
	S_2—S_C^*	163.2	3.0	6.9
	S_C^*—I	192.2	5.3	11.4
14	C—S_2	123.5	13.6	34.2
	S_2—S_C^*	160.3	3.1	7.0
	S_C^*—I	190.3	5.8	12.5

[a] Transition only observed by D.S.C.
[b] Temperature of transition determined by optical microscopy.

In Figure 1, it can be seen that a variation of the melting temperatures as a function of the terminal chain length is only a consideration when passing from $n = 4$ to $n = 6$. The melting points vary minimally for the remaining homologues, being about 40–45° higher for compounds with $n = 2$ and 4 than for compounds with $n = 6$, 8, 10, 12, and 14. The clearing temperatures decrease down to $n = 6$ and then remain almost constant up to $n = 14$.

The ferroelectric properties of one of these compounds ($n = 10$) are currently being studied and the results will be reported.

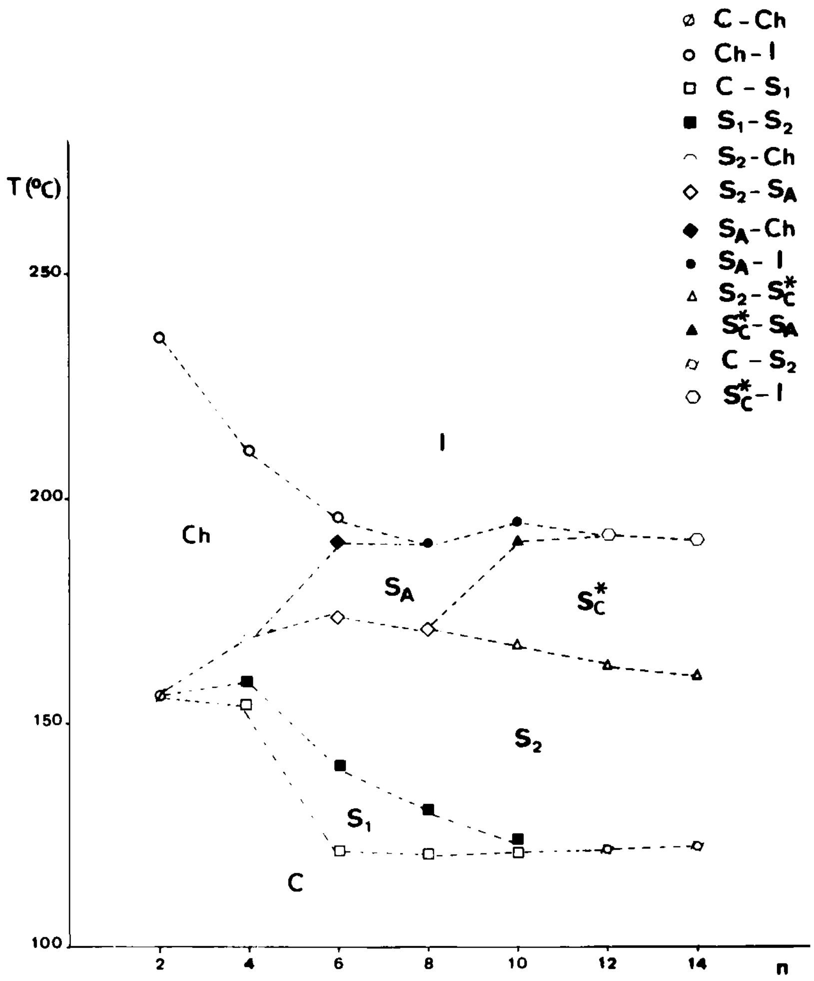


FIGURE 1 Transition temperatures as a function of alkoxy chain length for the compounds in the series.

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