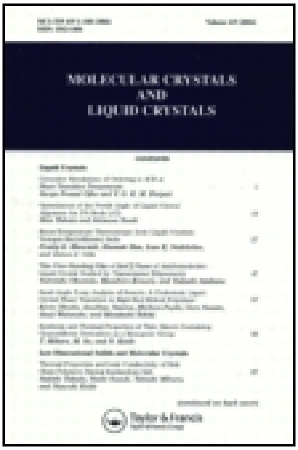

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Chiral Mesogenic Compounds: Carbocyclic and Heterocyclic Schiff Bases

J. Barbera [a] , E. Melendez [a] , J. L. Serrano [a] , M. T. Sierra [a] , A. Ezcurra [b] & M. A. Perez Jubindo [b]

[a] Química Orgánica, Facultad de Ciencias, Instituto de Ciencia de los Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., 50009, Zaragoza (España)

[b] Departamento de Física Aplicada II, Facultad de Ciencias, Universidad del Pais Vasco, Apdo. 644, 48080, Bilbao (España)

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Chiral Mesogenic Compounds: Carbocyclic and Heterocyclic Schiff Bases

J. BARBERA, E. MELENDEZ, J. L. SERRANO and M. T. SIERRA

Química Orgánica, Facultad de Ciencias, Instituto de Ciencia de los Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., 50009 Zaragoza (España).

and

A. EZCURRA and M. A. PEREZ JUBINDO

Departamento de Física Aplicada II, Facultad de Ciencias, Universidad del País Vasco, Apdo. 644, 48080 Bilbao (España).

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Five different chiral *p*-substituted anilines derived from 4-aminobenzoic acid and from 4-aminophenol were condensed with four carbocyclic and heterocyclic aldehydes in order to obtain chiral Schiff bases resembling DOBAMBC[1] and HOBACPC.[2]

With the exception of the pyridine-3-carboxaldehyde derivatives, the compounds are mesomorphic. Some of the compounds exhibit ferroelectric S_{C*} phases, and all exhibit S_A or Ch mesophases on heating. Benzaldehyde and pyridine-2-carboxaldehyde derivatives show similar mesomorphic behavior, as was to be expected from MNDO semiempirical calculations.

Values of the spontaneous polarization of certain compounds were measured.

INTRODUCTION

In a previous paper,[3] we reported a study of chiral heterocyclic and carbocyclic compounds analogous to DOBAMBC,[1] which was taken as a structural model. It was the first time that pyridine-2- and -3-carboxaldehydes had been used as precursors to chiral Schiff bases with ferroelectric properties.

In this paper we extend the study of the influence of different types of ring in the aldehyde part of the molecule on the mesomorphic behavior of chiral Schiff bases. Accordingly, we have synthesized and studied twenty compounds, the structures of which are shown in Figure 1. In four cases the value of *Ps* has been measured.

Compound Ia has been previously reported in the literature,[4] but in order to ensure an accurate comparative study, we prepared this compound and determined its thermal and thermodynamic properties, and its *Ps* value.

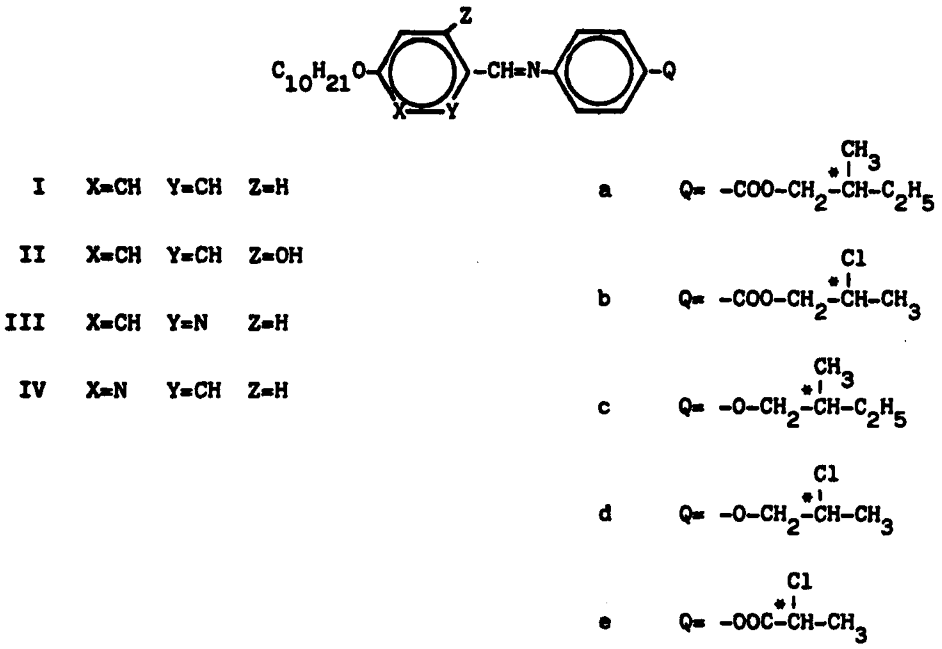

FIGURE 1 Structures of the Schiff bases synthesized.

RESULTS AND DISCUSSION

Description of the mesomorphic properties

The transition temperatures, enthalpies and nature of the mesomorphic phases of the compounds are gathered in Table I.

As can be observed, all compounds derived from benzaldehyde (type **I**), 2-hydroxybenzaldehyde (type **II**) and pyridine-2-carboxaldehyde (type **III**) are mesomorphic, exhibiting a S_A phase in most cases.

Potentially ferroelectric chiral mesophases (S_{C*}) appear in seven cases (compounds **Ia**, **IIIa**, **Ic**, **IIc**, **IId**, **Ie**, **IIIe**). In addition to the S_{C*} phase, compound **IIc** shows a chiral nematic phase (Ch). It is the only case in which the S_{C*} phase does not show an S_A phase at a higher temperature.

The 2-hydroxybenzaldehyde derivatives (**II**) show higher clearing points than the other compounds in all series, exhibiting S_A phases in most cases. On the other hand, the pyridine-3-carboxaldehyde derivatives (**IV**) do not show mesophases, with the exception of compound **IVb**, which has a monotropic S_A phase. The predominance of S_A and S_{C*} mesophases in the benzaldehyde (I) and pyridine-2-carboxaldehyde (III) derivatives is also noticeable. These results confirm our predictions based on MNDO calculations,[3,5] which conclude that the dipole moment direction determines the appearance of one type of mesophase or another. According to the MNDO calculations, the dipole moment lies at an oblique angle to the molecular axis in Schiff bases derived from benzaldehyde and pyridine-2-carboxaldehyde, and this favors smectic C phases. On the other hand, the dipole

TABLE I

Transition temperatures and enthalpies for the compounds synthesized.

Compound	Transition	T°C	ΔH Kcal/mol
Ia	$C-S_A$	47.6	6.2
	S_A-I	63.9	1.0
	S_A-S_{C*}(m)	40.5	
IIa	$C'-C$	65.5	0.3
	$C-S_A$	73.1	5.3
	S_A-I	84.2	1.0
IIIa	$C-S_A$	47.4	6.5
	S_A-I	69.4	1.0
	S_A-S_{C*}(m)	47.0	
IVa	$C-I$	50.1	8.9
Ib	$C-S_A$	55.6	8.9
	S_A-I	85.0	1.0
IIb	$C-S_A$	86.1	11.3
	S_A-I	112.0	1.2
IIIb	$C-S_A$	72.4	7.3
	S_A-I	85.8	0.9
IVb	$C-I$	59.2	10.7
	$I-S_A$(m)	58.7	0.8
Ic	$C-I$	83.8	10.6
	$I-S_A$(m)	81.2	1.2
	S_A-S_{C*}(m)	79.5	
IIc	$C-S_{C*}$	50.7	7.3
	$S_{C*}-Ch$	86.2	0.5
	$Ch-I$	88.2	0.5
IIIc	$C'-C$	50.5	0.9
	$C-S_A$	65.0	6.6
	S_A-I	75.2	1.1
IVc	$C-I$	77.4	10.6
Id	$C-S_A$	89.5	11.7
	S_A-I	95.2	1.0
	S_A-S_3(m)	76.9	0.6
IId	$C-S_{C*}$	60.4	11.2
	$S_{C*}-S_A$	62.4	
	S_A-I	116.8	1.5
IIId	$C-S_A$	57.3	10.0
	S_A-I	80.5	1.1
IVd	$C-I$	78.1	11.4
Ie	$C-S_A$	99.6	
	S_A-I	102.5	10.5
	S_A-S_{C*}(m)	90.0	
IIe	$C-S_A$	81.1	11.2
	S_A-I	103.4	0.8
IIIe	$C-S_A$	61.4	10.3
	S_A-I	87.4	1.1
	S_A-S_{C*}(m)	60.4	
IVe	$C-I$	96.3	11.8

$S_{C*}-S_A$ transition only observed by optical microscopy (m) monotropic transition.

moment is approximately perpendicular to the molecular axis in Schiff bases derived from pyridine-3-carboxaldehyde, and this obstructs the formation of tilted smectic phases.

The 2-hydroxybenzaldehyde derivatives (**II**) are a special case, because of the hydrogen bond between the —OH group and the imine linkage[6,7]; this affects not only the dipole moment, but also other molecular properties such as the extent of conjugation and molecular geometry.

Spontaneous polarization

Values of the spontaneous polarization for four of the seven compounds which show S_{C*} phases, have been measured.

Figures 2, 3, 4, and 5 show the *Ps* values of compounds **Ia**, **IIIa**, **IId**, and **IIIe**. The *Ps* values of the other compounds -**Ic**, **IIc**, and **Ie**- could not be measured by our method because the values are < 0.1 nC/cm^2.

The *Ps* value of compound **Ia** differs from that obtained by Kitamura *et al.*,[4] who measured the *Ps* of this compound for the monotropic S_{C*} phase supercooled until 5°C below the transitions S_A–S_{C*}. In our case, we could not keep the product in the monotropic phase S_{C*} at more than 2°C below this transition.

As can be observed by comparing the *Ps* value of compound **Ia** (*Ps* = 0.35) with that of compound **IIIa** (*Ps* = 3) and of compound **Ie** (*Ps* < 0.1) with that of compound **IIIe** (*Ps* = 8), the presence of a heterocycle in the molecule favors higher *Ps* values. This may well be due to the partial dipole moment which the heteroatom contributes to the molecular dipole moment.

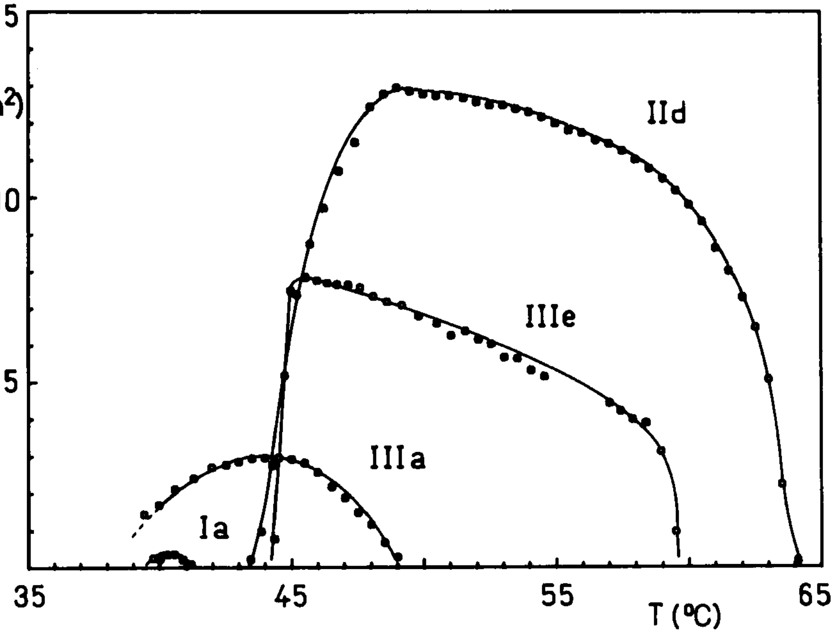

FIGURE 2 Temperature dependence of the polarization of compounds **Ia**, **IIIa**, **IId**, and **IIIe** in the S_{C*} phase.

Of all the materials measured, the best *Ps* is for compound **IId**, which has a *Ps* value of 13 nC/cm^2, comparable to that of HOBACPC.[2] Furthermore, this compound shows considerable stability when electric fields are applied.

EXPERIMENTAL

Synthesis

The chiral Schiff bases were synthesized from the appropriate aldehydes and chiral anilines.

Preparation of aldehydes. 4-Decyloxybenzaldehyde and 4-decyloxy-2-hydroxybenzaldehyde were alkylated using K_2CO_3 and $KHCO_3$, respectively, as bases and acetone as a solvent. The mixtures were heated for 48 h, and the products purified by column chromatography (toluene as eluant).

5-Decyloxypyridine-2-carboxyaldehyde was prepared by *O*-alkylation of 5-hydroxy-2-methylpyridine and oxidation of the methyl group by the action attack of iodine and dimethylsulfoxide as reported previously.[8]

6-Decyloxypyridine-3-carboxaldehyde was prepared by the action of sodium decyloxide on 6-chloronicotinic acid, followed by catalytic reduction of the acid to the aldehyde *via* the acid chloride according to the method described in a previous paper.[9]

Preparation of the chiral anilines. 4-Nitrobenzoate esters were prepared from 4-nitrobenzoic acid by esterification with the appropriate chiral alcohol in pyridine, followed by purification by column chromatography (toluene as eluant).

4-Alkoxynitrobenzenes were prepared from 4-nitrophenol by *O*-alkylation with the tosylate of the appropriate chiral alcohol, using K_2CO_3 as base and cyclohexanone as solvent. The mixture was heated for 2 h, and the products were purified by column chromatography (toluene as eluant).

4-Nitrophenyl 2-chloropropanoate was prepared by esterification of 4-nitrophenol with 2-chloropropanoyl chloride in methylene chloride/pyridine at room temperature. The product was purified by column chromatography (toluene as eluant).

Reduction of the nitro-group was carried out using the Bellamy method,[10] with $SnCl_2 \cdot 2H_2O$ in ethanol and under a N_2 atmosphere. The amines obtained were used without further purification.

Preparation of chiral alcohols. The chiral alcohols used were S(-)-2-methylbutanol and R(-)-2-chloropropanol. The former was purchased and the latter was prepared from L(+)-lactic acid by nucleophilic substitution of the hydroxy group by chlorine,[2] followed by reduction of the R(-)-2-chloropropanoic acid with $LiAlH_4$ in ether.[11]

Preparation of Schiff bases. The twenty Schiff bases were obtained from the appropriate aldehyde and amino-compounds using ethanol/acetic acid at room temperature. The products were purified by crystallization from methanol.

Measurement of *Ps*

The spontaneous polarization, *Ps*, was obtained by using the triangular wave method.[12,13] The saturated current-voltage (I-V) cycles were recorded by a digital acquisition system HP7090a. The *Ps* values were obtained from the depolarization contribution of the helical reorientation to the total current. The frequency was set at 50 Hz and *Ps* was taken as the value for V = 0 in the integrated hysteresis loops. All the equipment was interfaced to a microcomputer.

Cells for the above-mentioned measurements were made with gold-brass electrodes and an annular teflon ring 120 μm thick as spacer. The measurements were performed on homogeneously aligned samples.

Textures observed

The mesophase textures were observed using thin films of the samples (mounted between a glass slide and a cover slip) and a polarizing microscope.

The chiral mesophases of type S_{C*} were identified by their similarities to the textures photographed by Gray and Goodby.[14]

The S_3 mesophase in compound **Id** is a tilted mesophase, but unidentified at the moment.

Techniques

The melting points, transition temperatures and enthalpies were determined using a Perkin-Elmer DSC-2 Differential Scanning Calorimeter. The heating rate was 5 K/min. The apparatus was calibrated by measuring the known melting point and heat of fusion of indium (156.6°C, 6.8 cal/g.) and tin (231.9°C, 14.45 cal/g.).

The optical observations, and the determination of $S_{C*}-S_A$ transition temperatures were made using a Polarizing Microscope equipped with a heating stage Mettler FP 82.

The identification of products was carried out by the usual spectroscopic methods: u.v. (Perkin-Elmer 200), i.r. (Perkin-Elmer 283) and n.m.r. (Bruker wp-80-SY).

CONCLUSIONS

All the derivatives of benzaldehyde (**I**), 2-hydroxybenzaldehyde (**II**) and pyridine-2-carboxaldehyde (**III**) that have been studied are mesomorphic, whereas most of the pyridine-3-carboxaldehyde derivatives are not. The 2-hydroxybenzaldehyde derivatives show higher clearing points in all cases.

In all the compounds which show mesomorphism, the S_A phase predominates, and a S_{C*} phase also appears in seven cases. The S_{C*} phase appears mainly in benzaldehyde (**I**) and pyridine-2-carboxaldehyde (**III**) derivatives, confirming MNDO predictions.

The *Ps* values of four of the seven compounds exhibiting S_{C*} phases have been measured. The highest *Ps* value is for 4-(2-chloropropyloxy)-*N*-(4-decyloxy-2-hydroxybenzylidene) aniline.

It is noted that the pyridine-2-carboxaldehyde derivatives show higher *Ps* values because of the dipole moment stemming from the heterocycle in the molecule.

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