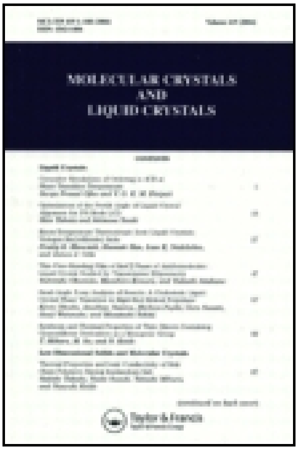

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Synthesis and Properties of Thermotropic Liquid Crystals with Two Non-Mesogenic Units and a Flexible Central Spacer

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Synthesis and Properties of Thermotropic Liquid Crystals with Two Non-Mesogenic Units and a Flexible Central Spacer

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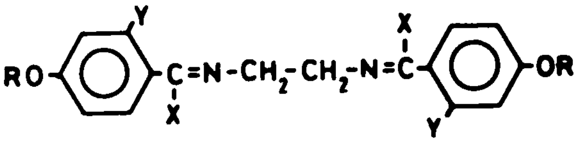
The synthesis of new di-Schiff bases with two non-mesogenic units and a flexible central spacer (—CH_2—CH_2—) in their structure is reported. The mesomorphic properties of the compounds were investigated by differential scanning calorimetry (DSC) and polarizing microscopy.

The Schiff bases derived from the aldehydes were mesogenic while those derived from the ketones were not. A comparative study of their different mesogenic behavior was carried out to establish the influence of molecular structure on liquid crystal properties.

INTRODUCTION

The possibility of extending conjugation along the rigid central core of a molecule has traditionally been considered an important requirement for the mesogenic behavior.[1] Very few mesogenic compounds which possess a flexible middle group are reported in the literature. Normally this flexible middle group either joins two mesogenic units[2,3,4] or one mesogenic and one non-mesogenic unit.[5] In fact Eidenschink[6,7] pointed out that molecules with a polar–nonpolar–polar sequence have a suppressed liquid crystal behavior.



R = C_nH_{2n+1}

Series I   Y = X = H

Series II   Y = H ; X = CH_3

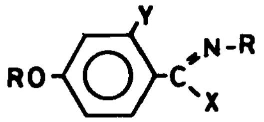
Series III   Y = OH ; X = H

Series IV   Y = OH ; X = CH_3

As a result of our search for an exception to the rule, we present our results concerning the synthesis and liquid crystal properties of several Schiff bases which possess a flexible middle group between two non-mesogenic units (Sketch 1).

A comparative study of the mesomorphic behavior of these series has been carried out using the decyl member in order to study: *a*) the influence of the hydroxyl group in position 2 of the aromatic rings; and *b*) the influence which the presence or absence of a methyl group in the imine central core has on the liquid crystal properties of the compounds.

In order to show that the aromatic part of the molecule is not, alone, responsible for the mesogenic properties of the compounds we synthesized and studied four model compounds (the decyl members) with the following structure, Sketch 2.



$R = C_{10}H_{21}$

Ia/ $X = Y = H$

IIa/ $X = CH_3$; $Y = H$

IIIa/ $X = H$; $Y = OH$

IVa/ $X = CH_3$; $Y = OH$

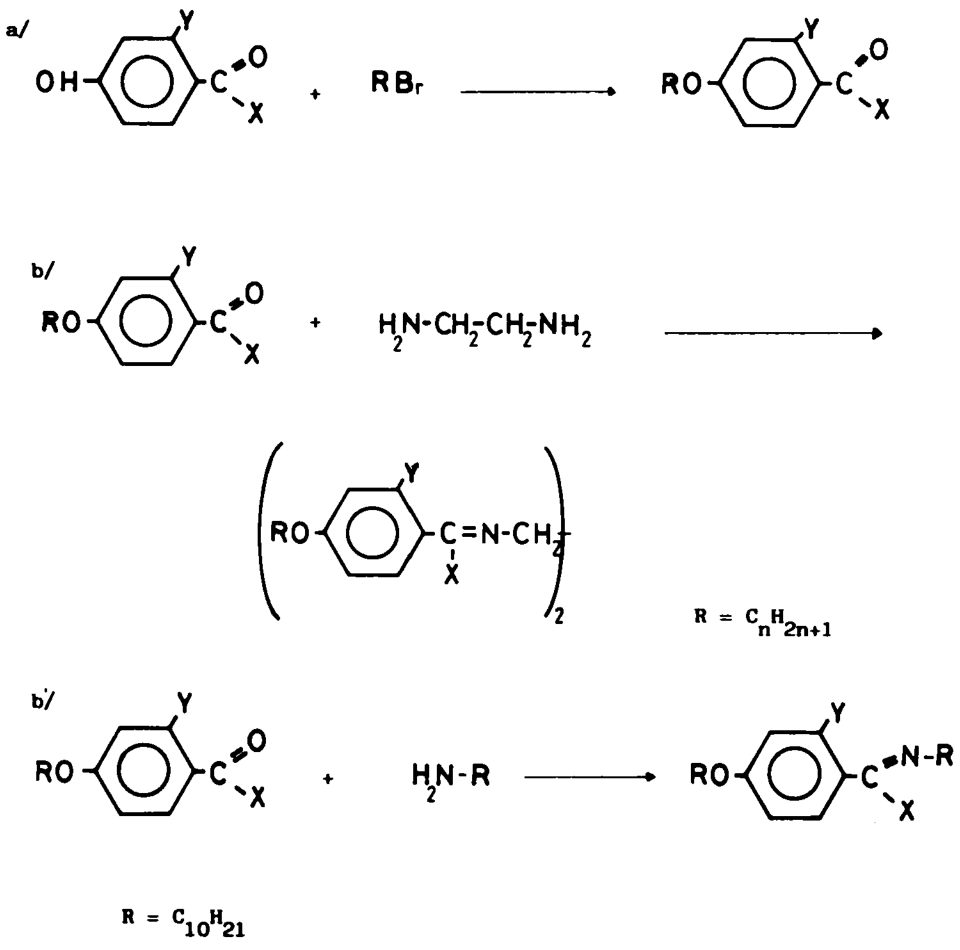
EXPERIMENTAL

Synthesis of compounds

The compounds were prepared following the route shown in Scheme 1 using methods similar to those in the literature:
a) alkylation of the OH group using the Williamson method[8,9]; *b*,*b*′) preparation of Schiff bases by condensing the carbonyl compounds with *b*) 1,2-diaminoethane, *b*′) decylamine, using ethanol and two drops of acetic acid as catalyst for the aldehydes and toluene and 4-toluenesulfonic acid in a Dean-Stark apparatus for ketones.

Physical methods

Transition temperatures and enthalpies were measured by differential scanning calorimetry (Perkin-Elmer DSC-2) at a scanning rate of 10 K/min on heating. The apparatus was calibrated with indium (429.9 K, 6.8 cal/g) and tin (505.06 K, 14.45 cal/g) as standards.



SCHEME I

The textures of the mesophases were studied with a Meiji polarizing microscope equipped with a heating stage Mettler FP 82.

The identification of products was carried out by the usual spectroscopic methods: UV (Perkin-Elmer 200); IR (Perkin-Elmer 283) and NMR (Bruker wp-80-sy).

The purity of all products was checked by the above mentioned techniques and C, H and N analysis (Perkin-Elmer 240 B microanalyzer).

RESULTS AND DISCUSSION

Properties of the model compounds

Transition temperatures and phase transition types for the four model compounds are in Table I. None showed mesomorphic properties.

TABLE I

Optical and thermal data for the model compounds (Sketch 2)

X	Y	Transition	Temperature (°C)
H	H	C–I	33.2
CH_3	H	C–I	51.3
H	OH	C–I	39.0
CH_3	OH	C–I	62.3

These results confirm that the aromatic part of the molecules is not able to generate mesomorphic properties in these compounds.

Study of mesomorphic properties of compounds in series I, II, III and IV

Transition temperatures, enthalpies and the phase types of the different compounds of series I, II, III and IV are in Tables II and III.

As we can see in Table II, the compounds of series II and IV (derived from the ketones), where *R* = $C_{10}H_{21}$, did not show mesomorphic behavior. The compound of series I (derived from an aldehyde), where R = $C_{10}H_{21}$, shows a monotropic nematic phase (this result differs from data reported by Vora et al.[2] who state that this compound is not mesomorphic), and the compound of series III exhibited enantiotropic Smectic C behavior.

Because of the poor mesomorphic properties observed for the decyl members of series I, II and IV, we limited our study to the effect of increasing terminal chain length in the compounds of series III.

TABLE II

Optical, thermal and thermodynamic data for the decyl members of series I, II, III and IV (Sketch 1)

Compound	X	Y	Transition	Temperature (°C)	ΔH (KJ/mol)
I	H	H	C–I	81.7	85.53
			I–N	(70.6)[a]	9.29
II	CH_3	H	C_1–C_2	73.2	2.43
			C_2–I	126.8	72.90
III	H	OH	C_1–C_2	57.1	22.20
			C_2–S_C	84.0	33.65
			S_C–I	105.8	16.26
IV	CH_3	OH	C_1–C_2	152.7	13.36
			C_2–C_3	155.0	38.57
			C_3–I	164.0	14.02

[a](□) = Monotropic transition.

TABLE III

Optical, thermal and thermodynamic data for *N*,*N*-di-(4-*n*-alkoxy-2-hydroxybenzylidene)1,2-diaminoethane (series III).

n	Transition	Temperature (°C)	ΔH (KJ/mol)
3	C–I	101.1	37.83
4	C–I	122.4	64.87
5	C–I	85.3	57.98
6	C–I	104.3	65.26
	I–S_C	(89.3)[a]	10.09
7	C_1–C_2	51.3	3.23
	C_2–S_C	82.3	32.09
	S_C–I	97.9	12.41
8	C_1–C_2	66.3	10.33
	C_2–S_C	87.2	27.15
	S_C–I	103.2	13.77
9	C_1–C_2	70.8	35.99
	C_2–C_3	72.3	35.99
	C_3–S_C	78.4	20.65
	S_C–I	103.4	15.75
10	C_1–C_2	57.1	22.20
	C_2–S_C	84.0	33.65
	S_C–I	105.8	16.26
12	C_1–C_2	68.4	8.34
	C_2–C_3	81.0	54.92
	C_3–S_C	84.6	43.70
	S_C–I	106.1	20.04
14	C_1–C_2	74.5	6.33
	C_2–S_C	90.3	67.22
	S_C–I	106.1	20.04
15	C_1–C_2	57.1	3.19
	C_2–S_C	96.6	101.96
	S_C–I	103.4	4.63
16	C_1–C_2	77.4	7.87
	C_2–S_C	97.3	74.50
	S_C–I	104.1	12.16

[a](☐) Monotropic transition.

Influence of the OH group in the *ortho*-position on the mesogenic properties

The compound in series I (n = 10) shows monotropic nematic behavior, whereas the compound in series III (n = 10) shows an enantiotropic S_c phase (see Table I).

The different behavior is caused by the introduction of the hydroxyl group in the *ortho*-position for the compound in series III. This hydroxyl group forms an intramolecular H-bond of considerable strength with the nitrogen in the imine, forming a six-membered chelate ring and producing some fundamental effects on the molecules: *a*) a reduction of the rotational motions within the molecule, *b*) an increase in the planarity of this part of the molecule, and, consequently *c*) an increase in the polarizability of the molecule.

These effects lead to greater chemical and liquid crystalline stability of the compounds of series III.

These results are similar to those observed for certain other compounds with similar structures.[10–14]

Effect of increasing terminal chain length of series III

As we observe in Figure 1, the compounds in series III do not show liquid crystal behavior for $n = 3,4,5$, but they do show an enantiotropic Smectic C phase for $n = 7-10$, 12, 14, 15, and 16, and, when $n = 6$, a monotropic S_c phase.

Systematic studies of homologous series of mesogenic compounds in which the terminal substituent (alkyl or alkoxy groups) is lengthened show that, in general, the behavior exhibited is a nematic mesophase for short terminal chains and smectic properties for the longest chains, while intermediate lengths of the terminal chain give both smectic and nematic mesophase. However, some systems only exhibit smectic behavior or nematic properties. Such effects have been discussed fully by Gray.[15]

The type of order that appears depends on the forces which predominate after fusion, smectic ordering being favored by lateral intermolecular attractions and nematic ordering by terminal intermolecular attractions.

The compounds studied only show smectic phases, which means that lateral intermolecular attractions between the polarizable core parts predominate in this type of molecule. These forces originate from dipole–dipole and induced dipole

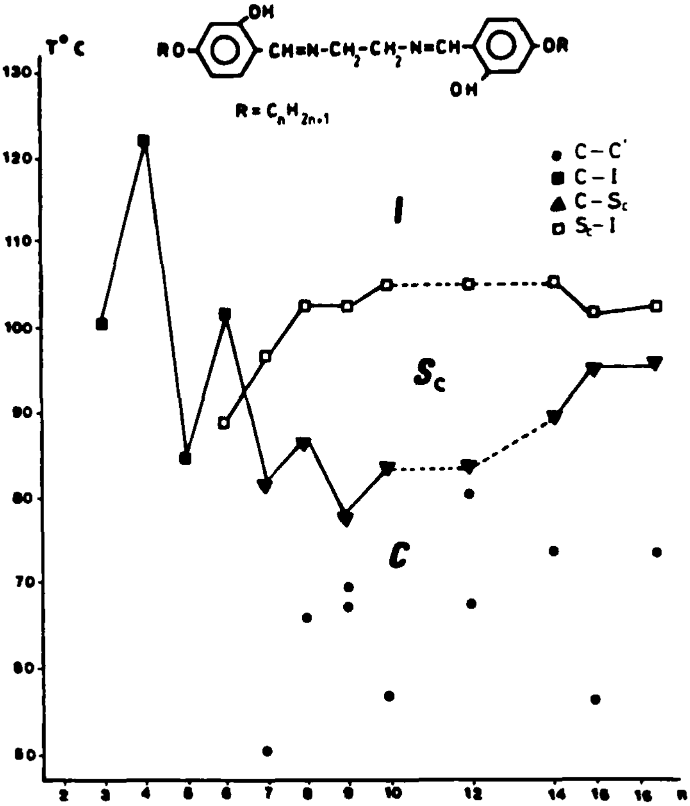


FIGURE 1 Dependence of transition temperatures of the compounds in series III on the length of the terminal chain.

interactions. These interactions, together with the length of the molecule, make misalignment of the molecules more difficult and maintain the material in the smectic phase after fusion has occurred.

It is noteworthy that only the Smectic C phase appears in these compounds, and this could be accounted for by applying McMillan's dipole model[16] for the Smectic C mesophase. The molecules are symmetrical in shape and have lateral/outboard dipoles associated with the ends of the central core structure in accordance with the requirements of his model. (See Figure 2)

In a previous study,[17] we demonstrated by means of semi-empirical calculations of molecular orbitals (MNDO) that in molecules with the dipole moment perpendicular to the principal axis, the existence of orthogonal smectic phases (S_A, S_B, . . .) is observed, while in molecules where the dipole moment forms an oblique angle with the axis tilted smectic mesophases (S_C, S_G, S_H, . . .) generally appear.

In the all *trans*-configuration of the molecules of our compounds, the outboard dipoles of each half molecule are approximately antiparallel and their direction is tilted in relation to the axis of the half molecule.

This was also proved by MNDO studies using the model molecules A and B shown in Figure 3. (Model molecules had to be used in order to reduce the calculation time.)

The data corresponding to the total dipole moments (μ_T), the components ($\mu_\parallel$ and $\mu_\perp$), and the angles (θ) with the long axes of the molecules extracted from the theoretical calculations, are gathered in Figure 3. As can be seen, these results show that the dipole moments form an oblique angle with the main axis, which favors the appearance of S_C mesophase in the compounds.

When $n = 3, 4, 5$ mesomorphic properties are not shown by the compounds. According to Gray,[15] there are several reasons for such behavior:

a) If the intermolecular attractions are too strong, then the melting point of the crystal may be so high that liquid crystal properties are prevented after melting.

b) If the intermolecular forces are very weak, then although the crystal may melt at a low temperature, the cohesive forces will be inadequate to maintain the order in the fluid state.

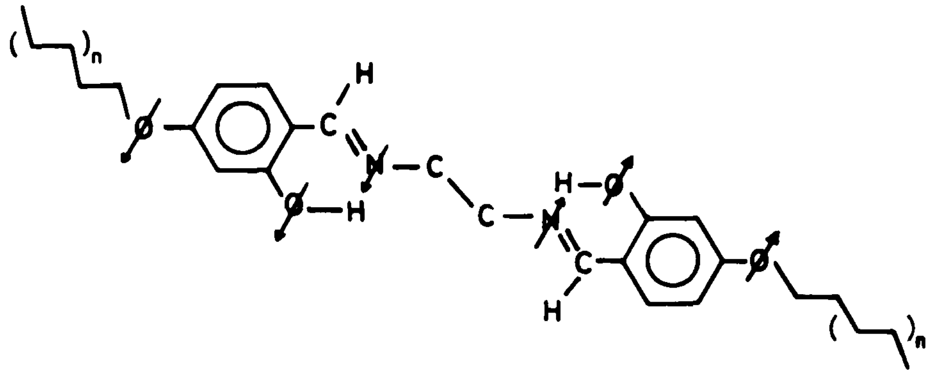
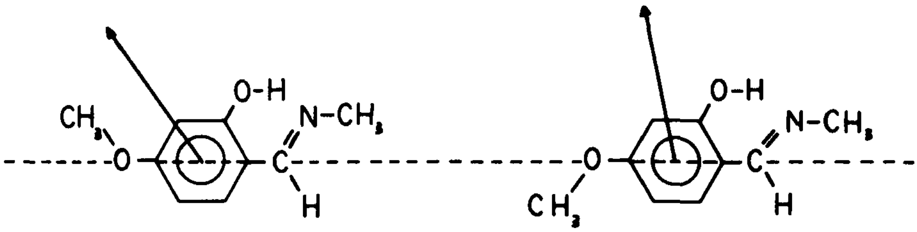


FIGURE 2



$\mu_x = -0.865$	$\mu_x = -0.670$
$\mu_y = -1.212$	$\mu_y = -3.428$
$\mu_z = -0.001$	$\mu_z = 0.001$
$\mu_T = 1.489$	$\mu_T = 3.492$
$\theta = 125.5$	$\theta = 101.1$

FIGURE 3 Model compounds used for MNDO studies.

c) If the molecule lacks rigidity, flexing may occur along its length and this may in itself prevent liquid crystal formation.

In our opinion, criterion *c*) would justify the non-appearance of mesomorphic behavior in the short members of the series studied here ($n = 3, 4, 5$), because the flexibility of the central linking moiety hinders a satisfactory molecular linearity in molecules with short terminal chains. This suggests that the length of the alkoxy terminal chain is also important in molecular interactions, and that beyond a certain length of alkoxy chain the advantage of better packing more than offsets the greater chain flexibility, and liquid crystal properties appear for $n \geq 6$.

As can be observed in Figure 1, the melting temperatures decrease as n increases, reaching a minimum when $n = 8$. A considerable odd–even effect is also observed.

Clearing temperatures gradually increase from $n = 6$, but a slight decrease is observed for $n = 15$ and 16. It can be seen in Figure 1 that all compounds in the series show crystalline polymorphism.

The solid state transitions observed by optical microscopy were:

$$C_1 \rightleftharpoons C_2 \rightleftharpoons S_C \quad \text{for} \quad n = 7, 8, 10, 14, 15, 16$$

$$C_1 \rightleftharpoons C_2 \rightleftharpoons C_3 \rightleftharpoons S_C \quad \text{for} \quad n = 9, 12$$

Differences in mesomorphic behavior between compounds derived from ketone and aldehydes

The fact that the compounds ($R = C_{10}H_{21}$) of series II and IV derived from ketones are not mesomorphic, whereas their analogues in series I and III are, is undoubtedly due to the methyl group in the imine structure (see Table II). The methyl group widens the molecules and makes close packing of the molecules difficult; this hinders the formation of liquid crystals by the compounds.

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