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New laterally aromatic branched liquid crystal materials with large nematic ranges

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New laterally aromatic branched liquid crystal materials with large nematic ranges

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Three new homologous series of mesogens containing three rings in the main structure and a lateral aromatic branch have been synthesized. When the lateral aromatic branch is attached to the middle ring, monotropic phases are observed, and there is a strong tendency to form the smectic C phase. When the lateral aromatic branch is attached to an outer ring, the compounds possess purely enantiotropic nematic phases. The terminal alkoxy chain in the outer ring which has a lateral aromatic substituent can be replaced by a rigid group without disturbing the large nematic range. Selective introduction of a particular substitutent may be useful for the construction of devices possessing desirable characteristics such as non-linear optical properties.

1. Introduction

Most thermotropic liquid crystals have a rigid core composed of two or more aromatic and/or aliphatic rings and one or more flexible terminal alkyl/alkoxy chains [1, 2]. In general, the rings are linked with 0, 2, 4 units, producing generally a rod-like, lathe-like or disc-like structure.

In general, a rigid, lateral substituent perturbs the orderings of liquid-crystalline phases [3–5], causing a significant depression in the clearing point, a reduction of the liquid crystal range, and a destabilization of ordered smectic phases. However, the effect of a lateral, flexible substituent like an alkoxy or alkyl chain is quite different [6–9]. A methyl or a methoxy substituent causes a strong decrease in the melting and clearing temperatures, but as the chain length increases, the effect of the perturbation diminishes. In fact, chains with three or more carbons perturb the molecular arrangement in the liquid-crystalline phase to about the same extent, as the lateral alkyl chain is supposed to be orientated along the long molecular axis. Until now, only compounds containing three rings have been shown to exhibit some liquid-crystalline properties if the lateral substituent is an alkyl or an alkoxy group.

The type of liquid-crystalline phases formed by these compounds depends mainly on the position of the lateral chain. The nematic phase is preferred if the lateral chain is attached to an inner ring, but smectic phases are favoured if the lateral and terminal chains are attached to an outer ring in the *meta* and *para* positions, respectively.

The effect of a lateral aromatic branch on the type of liquid crystals formed is not well-known, as only a few investigators have addressed this problem [10–12]. After the

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pioneering work of Weissflog and Demus [6], only lateral aromatic branches were introduced in the inner ring with or without the use of a spacer. In these cases both nematic and smectic phases have been observed. However, the effect of lateral aromatic branching in an outer ring on liquid crystal properties has not been reported.

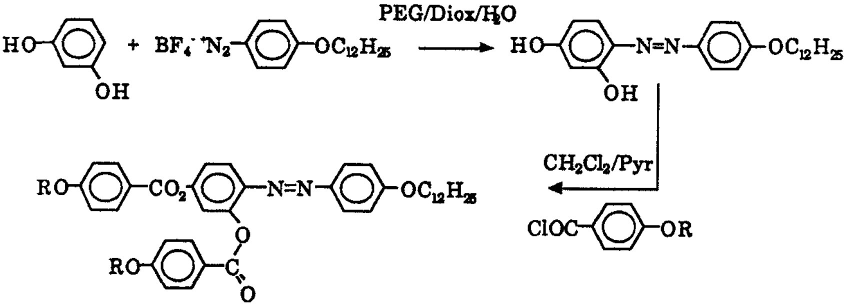
In this paper, we present the synthesis and properties of some compounds containing three rings in the main core and substituted by a lateral aromatic branch in either the central ring or one of the outer rings.

2. Experimental

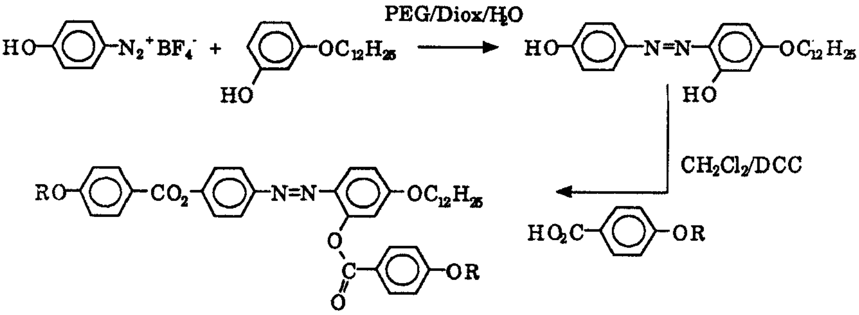
Three series of compounds were prepared according to the schemes shown below.

The preparation of the monoalkylated precursors involved the use of a mixture of polyethyleneglycol(MW 200)/dioxane and potassium hydrogen carbonate as base to accomplish selective etherification [13]. The detailed procedures of schemes 1–3 are given elsewhere [13]. Compounds of series I were purified by chromatography on silica gel, using pentane/chloroform (70/30) as eluent. Two recrystallizations from ethyl acetate/ethanol (15/85) produced pure compounds. Compounds of series II were recrystallized from chloroform/ethanol (20/80) until constant transition points were obtained, while compounds of series III were recrystallized from toluene/ethanol (30/70) until constant transition points were obtained.

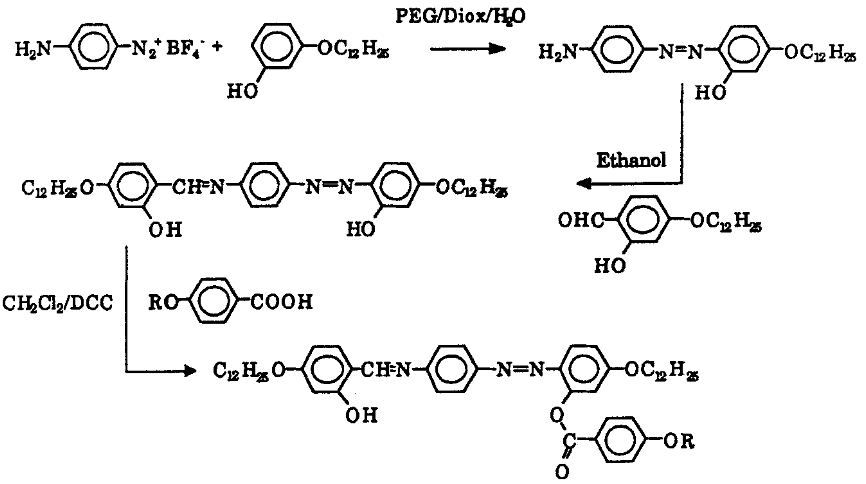
The structures of all the products were verified using ^{1}H NMR using a AM 250 Bruker spectrometer and by mass spectrometry (R10-10C Nermag mass spectrometer).



Scheme 1. The synthesis of series I, 4-dodecyloxy-2'-(4-alkoxybenzoyloxy)-4'-(4-alkoxybenzoyloxy) azobenzenes.



Scheme 2. The synthesis of series II, 2-alkoxybenzoyloxy-4-dodecyloxy-4'-(4-alkoxybenzoyloxy)-azobenzenes.



Scheme 3. The synthesis of series III, 2-alkoxybenzoyloxy-4-dodecyloxy-4′-(4-alkoxysalicylaldimine)-azobenzenes.

Table 1. Transition temperatures (°C) of series I. Values in parenthesis are taken with decreasing temperature. C, crystal; S_C, smectic C; N, nematic; I, isotropic.

n	C	→	S_C	→	N	→	I
4	●	91·7					●
	●	(48·8)			●	(70·4)	●
8	●	79·4					●
	●	(23)			●	(71·4)	●
12	●	73·4					●
	●	(18·1)	●	(41·4)	●	(67·4)	●
16	●	72·1			●	77	●
	●	(27·7)	●	(66·7)	●	(74)	●

Their purity was monitored by thin layer chromatography (TLC). The phase transitions were observed and characterized by using a Leitz polarizing microscope fitted with a FP 84 Mettler heating stage and a FP 52 Mettler DSC.

Some of the phases were also confirmed by X-ray diffraction.

3. Results and discussion

3.1. *4-Dodecyloxy-2′-(4-alkoxybenzoyloxy)-4′-(4-alkoxybenzoyloxy)-azobenzenes (Series I)*

The transition temperatures of four compounds in this homologous series are given in table 1. All the compounds are monotropic nematogens with the exception of the last member.

Figure 1 shows the dependence of the transition temperatures on the number of atoms, *n*, in the terminal and the lateral substituents. The most striking feature is that there is essentially no dependence of T_{NI} on increasing number of carbon atoms in the chains. Usually the decrease in the clearing point is attributed to the dilution of the core induced by the increasing length of the terminal alkoxy chain. This effect appears to be

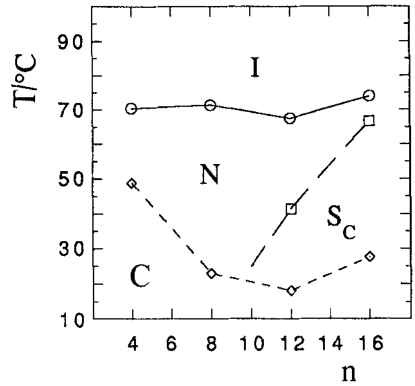


Figure 1. Phase behaviour for the homologous series I as a function of number of carbons (*n*) in the alkoxy chain. The transition temperatures were obtained on cooling by DSC.

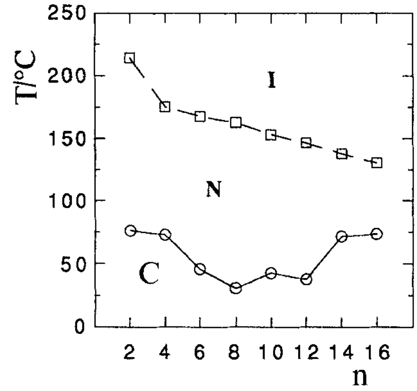


Figure 2. Phase behaviour for the homologous series II as a function of number of carbons (*n*) in the alkoxy chain. The transition temperatures were obtained on cooling by DSC. All the compounds are enantiotropic nematic.

minimized for the laterally substituted compounds I, as the lateral alkoxy chain partially overlaps the main core of the liquid-crystalline molecule.

In general, large lateral substituents hinder the packing in a layered structure and so depress the smectogenic properties; therefore the presence of the S_C phase with the increasing number of carbons in the lateral and terminal chains in this series is quite unusual. The lateral ring-containing substituent must play an important role in the stability of the smectic phase.

3.2. *2-Alkoxybenzoyl-4-dodecyloxy-4′-(4-alkoxybenzoyloxy)-azobenzenes.* (*Series II*)

The transition temperatures of the compounds in this series are given in table 2. All the compounds are enantiotropic nematogens. Figure 2 shows the dependence of the transition temperatures on the length of both the terminal and the lateral alkoxy chains. No smectic phase is observed. Therefore, it appears that the lateral substituent on the outer ring increases the dissymmetry of the molecule and does not allow the more ordered smectic phases to occur.

Table 2. Transition temperatures (°C) of series II. Temperatures on cooling are in parenthesis.

n	C	→	N	→	I
2	●	115·6	●	218·3	●
	●	(76·2)	●	(214·4)	●
4	●	115·3	●	188·3	●
	●	(72·7)	●	(175·4)	●
6	●	94	●	172·3	●
	●	(45·8)	●	(167·9)	●
8	●	91·3	●	164·2	●
	●	(30·5)	●	(162·5)	●
10	●	90·3	●	156·2	●
	●	(42·7)	●	(153·4)	●
12	●	83·9	●	149·8	●
	●	(37·7)	●	(146·4)	●
14	●	97·9	●	141·2	●
	●	(71·4)	●	(138)	●
16	●	98·9	●	132·7	●
	●	(73·5)	●	(130·5)	●

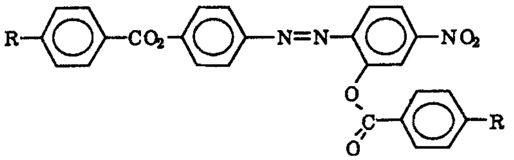
Table 3. Transition temperatures (°C) of the compounds IV. Temperatures on cooling are in parenthesis.

Comp.	C	→	S_A	→	N	→	I
A	●	127·6				>310	●
	●	(75·4)	●	(116·1)	●		●
B	●	79·2			●	235·1	●
	●	(66·2)			●	(234·9)	●

The nematic–isotropic transition temperatures of the compounds decrease smoothly with increasing chain length. This may be due to the dilution effect of the lateral alkoxy chain which is now located at the end of the molecule.

Since the two series I and II are isomeric, a comparison between them is of interest. The T_{NI} values of series II are higher than those of I by about 100°C for the first members and by 60°C for the last members. This clearly indicates the increased thermodynamic stability of the mesophase when the lateral substituent is moved from the inner ring to the outer ring.

In order to investigate the influence of the terminal chains in the main core, we have synthesized two compounds IV with a terminal nitro group, and their transition temperatures are listed in table 3.



IV

A: $R = OC_4H_9$ and B: $R = C_7H_{15}$

Compounds IV A exhibits on cooling both nematic and smectic A phases which are quite common for compounds bearing a terminal nitro group. This arises from interaction between molecules due to the dipole moment of the nitro group directed along the molecular long axis [14]. This interaction is present for compound IV A which bears a short chain with four carbons. If the chain length is increased, the interaction between the adjacent nitro groups is expected to be minimized. This behaviour is clearly demonstrated for compound IV B where the chains have seven carbons. A single nematic phase is observed over more than a 150°C range.

The introduction of a suitable substituent, such as nitro, in the hidden terminal position in these compounds is expected to enhance some desirable characteristics suitable for special applications, for example in non-linear optics. When the terminal alkoxy chains are sufficiently long, this substituent does not affect the phase type, and the compounds still have a large nematic range.

3.3. *2-Alkoxybenzoyloxy-4-dodecylocy-4′-(4-alkoxysalicylaldimine)-azobenzenes (Series III)*

It is known that the ester link is not a very good conjugative unit. We have therefore replaced it by an imino link in series III. This link has two major advantages: an increase in conjugation between the outer and the inner ring *via* an intramolecular hydrogen bond, and the salicylaldimine structure is able to complex metallic cations, possibly giving rise to metallomesogens [15].

The transition temperatures of the compounds in series III are given in table 4. All the compounds are enantiotropic nematics. Figure 3 shows the dependence of the transition temperatures on the number of carbon atoms in the alkoxy chain. The clearing points decrease slightly with temperature, similar to the behaviour in series II. Figure 4 gives the dependence of T_{NI} on the number of carbons for the two series II and III. For small values of n, compounds in series II have two short chains, but compounds in series III have only one short chain. Therefore, a comparison of the two series is most meaningful for larger values of n. The data in figure 4 show that for $n > 6$, values of T_{NI}

Table 4. Transition temperatures (°C) of series III. Temperatures on cooling are in parenthesis.

n	C	→	N	→	I
2	●	97·3	●	175·3	●
	●	(32·9)	●	(172·5)	●
4	●	107·4	●	175·2	●
	●	(62·8)	●	(170·4)	●
6	●	106·8	●	177·2	●
	●	(66·6)	●	(171·9)	●
8	●	92·8	●	172·2	●
	●	(44·7)	●	(171·4)	●
10	●	84·2	●	167·2	●
	●	(37·6)	●	(161·9)	●
12	●	88	●	155·2	●
	●	(33·3)	●	(148·9)	●
14	●	98·9	●	151·3	●
	●	(46·8)	●	(147·4)	●
16	●	98·1	●	156·3	●
	●	(62·5)	●	(142·4)	●

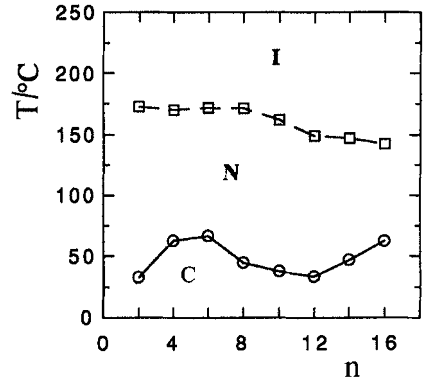


Figure 3. Phase behaviour for the homologous series III as a function of number of carbons (*n*) in the alkoxy chain. The transition temperatures were obtained on cooling by DSC. All the compounds are enantiotropic nematic.

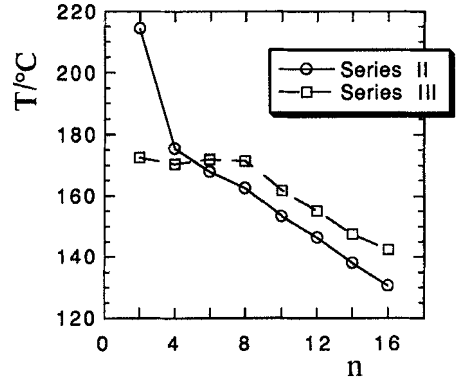


Figure 4. Comparison of the T_{NI} values for the homologous series II and III as a function of number of carbons (*n*) in the alkoxy chain.

for series III are above those for series II, confirming the stabilization of the mesophase induced by the conjugation. The decreases in T_{NI} with increasing chain length are quite similar for the two series.

4. Conclusions

We have described three different homologous series of mesogens, each composed of molecules containing three rings in the main core and having a lateral aromatic branch. The lateral aromatic branch is in the inner ring for one series and in the outer ring for the other two. The transition temperatures of these series are quite different, and the nematic range is dramatically increased if the lateral aromatic branch is attached to the outer ring.

We have shown that the terminal alkoxy chain in the ring with the lateral aromatic branch can be replaced by a rigid terminal group like nitro without disturbing the phase type and range. This property could be exploited for introducing some special groups into the main core structure without destroying the liquid-crystalline properties.

Other results on molecules with one or two lateral aromatic branches will be published separately [13].

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