



Article

New Liquid Crystals Based on Terminal Fatty Chains and Polymorphic Phase Formation from Their Mixtures

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Abstract: The physical and chemical properties of three new liquid crystalline derivatives, based on an azomethine core with low-temperature mesophase—namely (4-methoxybenzylideneamino) phenyl palmitate (**I**), (4-methoxybenzylideneamino) phenyl oleate (**II**), and (4-methoxybenzylideneamino) phenyl linoleate (**III**)—were prepared and physically examined using experimental methodologies. Elemental analysis, FT-IR, and NMR spectroscopy were used to confirm their molecular structure. Differential scanning calorimetry (DSC) and polarized optical microscopy (POM) were used to investigate their mesomorphic activity. The results revealed that compound (**I**) is monotropic smectogenic, possessing the smectic A mesophase, whereas the other two analogues were shown to possess the SmA phase enantiotropically. Two of the saturated and unsaturated prepared derivatives (namely **I** and **II**) were used to construct their phase diagram. The eutectic composition of the mixture examined showed a slight enhancement of the stability of the smectic A phase. Polymorphic phases were produced at the eutectic composition of the binary phase diagram of the derivative **II** with the 4-n-dodecyloxy benzoic acid component.

Keywords: mesomorphic properties; smectic phases; fatty acid liquid crystals; geometrical structures; binary phase diagram; polymorphic phases



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1. Introduction

It is well known that the physical properties of organic materials are largely determined by their molecular structure. Examining the structure–activity interactions is extremely useful when designing a material to achieve the necessary device applications [1–3]. Liquid crystals (LC) have been shown to be viable choices for device applications. Low-melting-temperature liquid crystals (LCs) have been proven to be useful materials for a variety of applications, including electro-optical displays and temperature sensors [4–9]. To be controllable in device applications, these materials must have particular features [4–6]. Optical transmittance, for example, influences the applicability of liquid crystalline substances. In addition, the mesophase type and stability are important traits. In the field of liquid crystal applications, color change with temperature is also a valuable phenomenon [10].

In general, LC compounds exhibit one or more different mesophases, such as nematic (N) and layered Smectic (Sm) phases, which are determined by their molecular order [11–13]. It has been shown that changes in the polarity and/or polarizability within the central core of the molecule can affect the mesophase stability of the prepared compound. Furthermore, the molecular structure of LC materials and, accordingly, their mesomorphic properties are

influenced by the terminal groups, which are either small, compact polar groups or flexible, lengthy hydrocarbon chains [14].

Mixtures of liquid crystalline (LC) materials are attracting great attention these days [15–21]. LC materials that show their transitions at room temperature and maintain their mesomorphic character throughout a large temperature range are desirable for practical applications. Mesomorphic requirements of mesogenic cores are significantly changed when individual components are mixed together. Many investigations [15–18] have focused on the mesophase behavior when two or more compounds are mixed where none, one, or all of the components are mesomorphic. Dimeric LCs have also been investigated [19–21]. Binary or ternary combinations can be composed of symmetric (mesogenic moieties are the same) or non-symmetric (mesogenic units are different) components. The intermolecular interaction between the two mesogenic cores of the two components of the mixture is accompanied with major changes in the optical activity of these materials in both molecules.

One of the important goals of our work is to perform a systematic investigation on the produced compounds that were attached with a linear *n*-alkyl chain of palmitic acid and unsaturated alkenyl chains (oleic and linoleic acids) with various degrees of unsaturation. Their good optical properties were previously confirmed by examining their mesomorphic behavior [6].

A new two-ring calamitic (I–III, Figure 1), with an azomethine group as a central linkage, was synthesized and its mesomorphic and optical behavior examined, aiming to obtain low melting temperatures in the range of room temperature. Another goal of the current study is to examine the mesomorphic and optical properties of binary mixtures, which were formed by mixing two systems with different terminal chains.

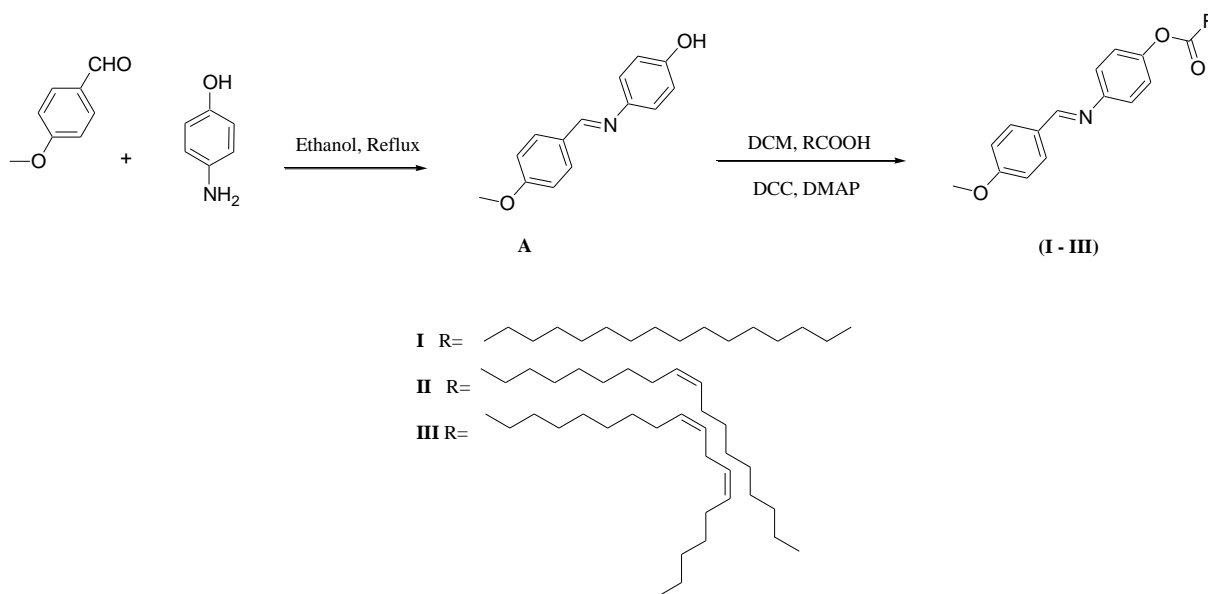


Figure 1. Synthesis of derivatives (I–III).

2. Experimental and Synthesis of Materials

Compounds I–III were prepared according to Figure 1. Synthetic method details are given in Supplementary data (S1–S4).

3. Results and Discussion

3.1. Mesomorphic Investigations

Table 1 shows the transition temperatures, enthalpy, and normalized entropy of transitions as measured by DSC. POM textures identify the phases for the prepared liquid crystal derivatives (I–III), which are confirmed by DSC measurements, with some typical textures shown in Figure 2. Figure 3a–c shows the DSC thermograms for all prepared derivatives (I–III) upon heating and cooling scan at a rate of 10 °C/min. The data in Table 1

and the phase transitions in Figure 4 show that all of the three synthesized derivatives are mesomorphic, with varying mesophase stability depending on the length and un-saturation of the alkyl or alkenyl chain. Furthermore, all of the prepared compounds were shown to possess the smectic A mesophase. When heated, (4-methoxybenzylideneamino) phenyl palmitate (**I**), which does not contain a double bond in its carbon terminal chain, is purely smectogenic, with a narrow monotropic smectic A phase range of near 9.8 °C. The length and unsaturation of the wing group in compound **II** [22], (4-methoxybenzylideneamino) phenyl oleate, was shown to affect their mesomorphic behavior, resulting in a SmA temperature range larger than that of the saturated analogue **I** (20.1 °C). In general, increasing the polarizability and/or polarity of the mesogenic component of the entire molecule improves mesophase stability. Compound **III** has a longer terminal chain compared to **I**, and two conjugated double bonds compared to its analogues **I** and **II**, which results in a further increase in the SmA temperature range (near 27.7 °C).

Table 1. Transition temperatures (T , °C), enthalpy of transitions (ΔH , kcal/mol), and normalized transition entropy ($\Delta S/R$) for compounds **I–III**.

Compound	T_{Cr-SmA}	ΔH_{Cr-SmA}	T_{SmA-I}	ΔH_{SmA-I}	ΔT_{SmA}	$\Delta S/R$
I	89.9	32.93	88.8 *	2.69	9.8 *	0.89
II	41.9	35.78	62.0	2.98	20.1	1.07
III	38.0	37.23	65.7	2.20	27.7	0.78

Abbreviations: Cr-SmA = crystal to smectic A transition; SmA-I = Smectic A to isotropic liquid transition. * monotropic phase on cooling only.



Figure 2. POM smectic A texture of the derivative **III** during heating scan at 50 °C.

The linoleic acid derivative **III** has a mesomorphic property, with a low melting point near room temperature (38.0 °C upon heating), as indicated from Table 1 and Figures 3 and 4. This is due to the length of the unsaturated alkenyl terminal chain. The strength of the terminal attractions causes the smectic molecular order to grow, allowing for the simple organization of the layers due to the long alkenyl chain, thereby expanding the SmA temperature range. The microphase separation between the aromatic cores and alkenyl chains, which becomes more advantageous as the terminal chain length grows, may also play a role in the creation of the smectic phase [23,24]. Many factors are known to influence the mesomorphic behavior of calamitic mesogens, including polarizability, dipole moment, aspect ratio, and competitive interactions within terminal aggregations. Furthermore, the molecular geometry is influenced by mesomeric configurations and has an impact on molecular–molecular interactions. According to our findings, the molecular aggregation of rod-like molecules caused by the lateral attraction of linear planar molecules with longer alkenyl chains may be the driving force behind mesophase activity. The end-to-end association of terminal flexible

chains, which varies depending on mesomeric effects, is another factor. The mesomorphic behavior is influenced by the combination of these factors in varying ratios. A major role of the alkenyl chains in terms of entropy is their liability; they can easily undergo multi-conformational changes [25]. As a result, the CH=N bond's thermal cis–trans isomerization can represent the lower entropy changes predicted for low-molar mass mesogens, which is consistent with other studies [26–29].

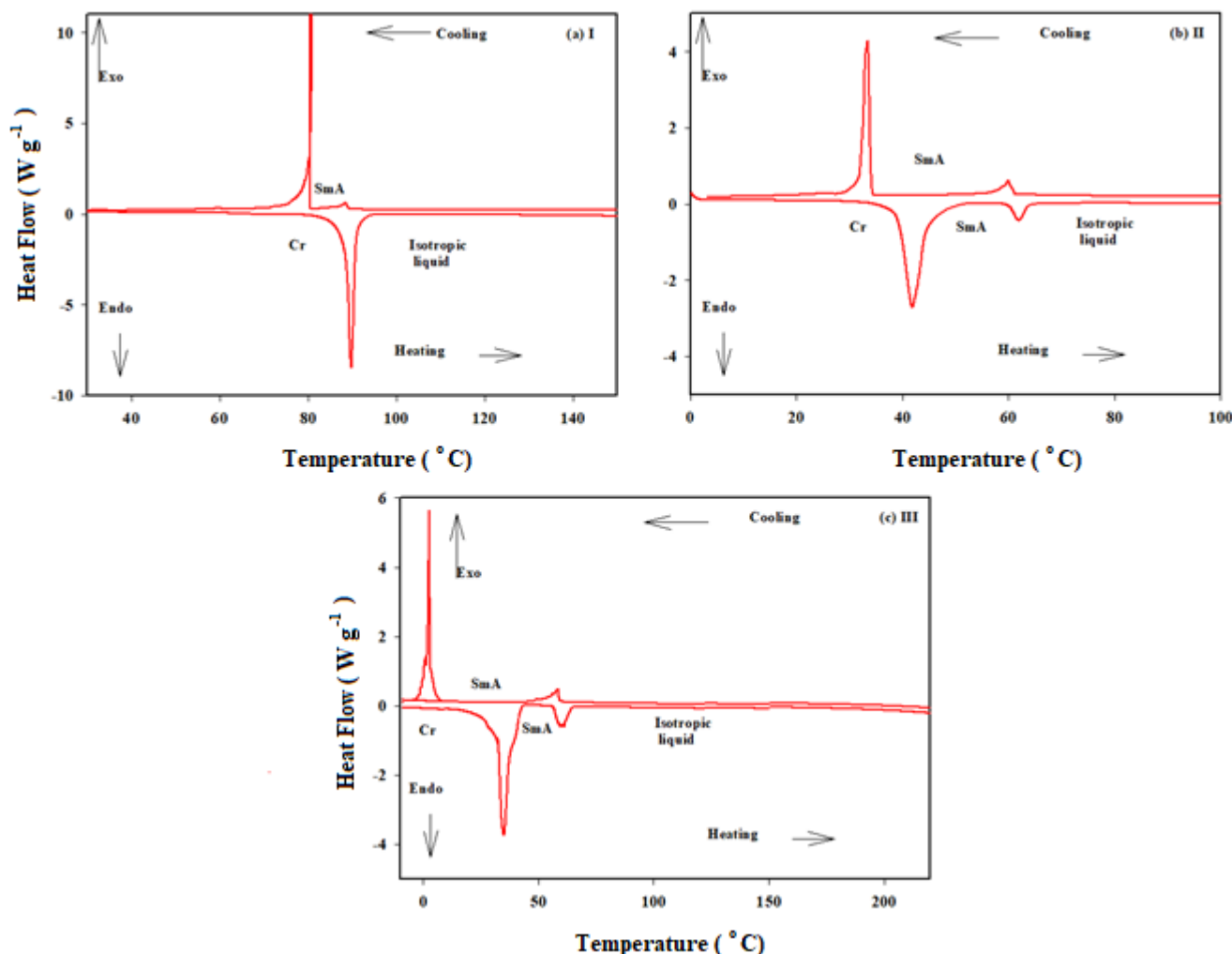


Figure 3. DSC thermograms upon second heating/cooling cycles of compounds (a) I, (b) II and (c) III with heating rate of 10 °C/min.

As can be seen from Figure 4, the inclusion of one or two double bonds is associated with a decrease in both the melting points and the smectic A stabilities. The difference between derivative I and either of the other two other derivatives, II or III, is two carbon atoms in the terminal chains, which does not significantly affect their mesophase behavior. Other differences are the single double bond in II and the two conjugated double bonds in III, which are far from the central mesogenic group that prevents the conjugation with the azomethine central linking group. The only possible reason for such a decrease in the stability of the smectic A phase is the possible non-linearity due to the cis–trans effect [6,21,29].

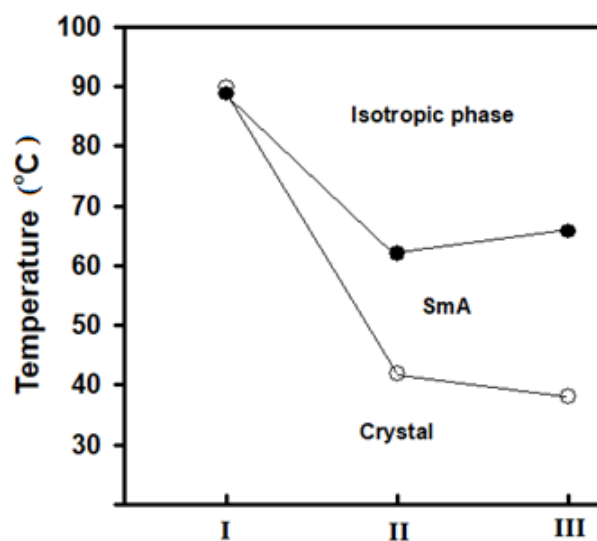


Figure 4. DSC phase transitions of prepared derivatives I–III.

3.2. Binary Mixtures

Figure 5 depicts the binary phase diagram produced from DSC measurements of two components, I and II, with different terminal chains. As can be seen from the diagram, over the entire composition range, the binary mixes were shown to exhibit the SmA mesophase. Derivative I exhibited the SmA phase monotropically, while compound II exhibited the SmA mesophase enantiotropically. The binary phase diagram shows a positive enhancement of the SmA phase compared to linear behavior, as shown in this diagram. This can be attributed to the variation in total lengths and different saturation between the two components of the mixture, which enhances the arrangement of the molecules. Furthermore, Figure 5 shows that the solid mixture with 22.0 mole % of I represents the eutectic composition, which melts at 40.0 °C and has a SmA temperature range of 29.1 °C. This is in accordance with previous investigations, where the length of the terminal chain determines both conformation and steric effect in pure and mixed states [6,15–18].

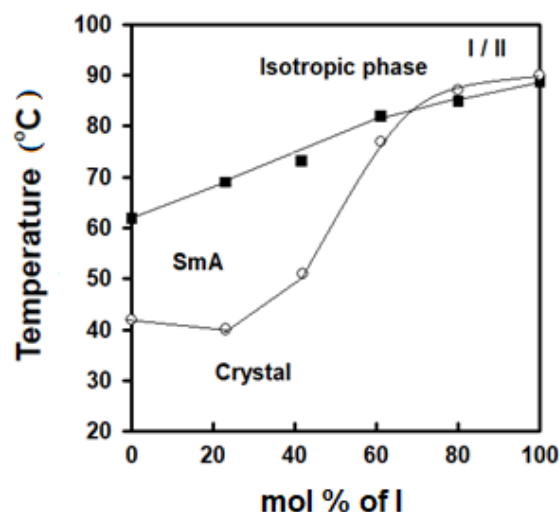


Figure 5. Binary phase diagram of I/II system.

Another example of a binary phase diagram was constructed for the present prepared fatty acid derivative II and the 4-n-dodecyloxy benzoic acid (D) in order to investigate the effect of different geometry of terminal chains on the mesomorphic properties of mixtures II/D. Figure 6 depicts a binary phase diagram obtained from DSC examinations of both components. The SmC and N mesophases are enantiotropically present in the alkoxy acid

derivative, **D**. The binary phase diagram shows a slight enhancement of the N phase over all compositions, as shown in this diagram. The enhancement of the N phase can be attributed to the good alignment between the two components (**II** and **D**) of the mixture, which does not disrupt the arrangement of the molecules. Moreover, polymorphic mesophases have been seen at eutectic point (41 mol% of **D**). Figure 6 further shows that the solid mixture with a 41.0 mol% eutectic composition of **D** has a eutectic melting point of 39.2 °C and a mesomorphic temperature range of 65.9 °C. Incorporation of one material with low melting temperature (**II**) in mixed states results in depression in the melting temperatures of all mixtures and leads to formation of polymorphic phases.

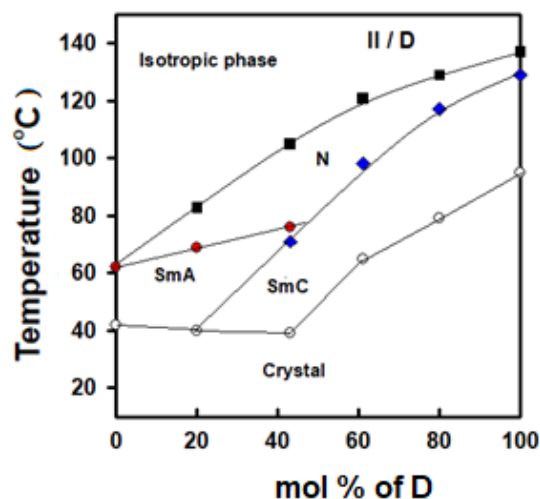
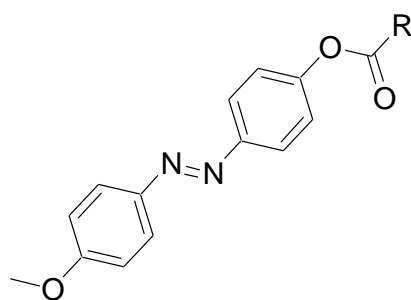


Figure 6. Binary phase diagram of **II/D** system; crystal-SmC transition (○); SmC-SmA (◆); SmA-N (●); N-isotropic (■).

3.3. Effect of Replacement of Azo Linkage by Azomethine Moiety

In order to investigate the effect of replacing the azo group with an azomethine one, the investigated compounds (**I–III**) are compared with those of the previously investigated azo analogues [6], 4-[2-(4-methoxy phenyl)diazenyl]phenyl hexadecanoate (**A**), 4-[2-(4-methoxyphenyl)diazenyl]phenyl octadeca-9-enoate (**B**), and 4-[2-(4-methoxy phenyl)diazenyl]phenyl octadeca-9,12-dienoate (**C**). Smectic A phase was also the mesophase observed in all of the azo compounds (**A–C**, Figure 7), but with lower transition temperatures compared with their azomethine analogues (**I–III**). It was found from the comparison between their mesophase stabilities that the azomethine derivatives (**I–III**) are of relatively higher thermal stability than the azo compounds (**A–C**). Thus, it seems that the attachment of $-\text{CH}=\text{N}$ -mesogen increases the polarizability and, consequently, enhances the intermolecular association between molecules, showing a higher stable phase. The results indicated that the type of linkage is more effective on the phase transitions and stability of designed compounds.



(**A–C**)

Figure 7. Azobenzene derivatives **A–C**.

4. Conclusions

In the present study, three liquid crystalline derivatives, based on natural fatty acids, were prepared and their mesomorphic behavior examined by DSC and POM. The results revealed that all of the synthesized saturated (I) and unsaturated (II and III) fatty acid analogues are monomorphic and possess the SmA mesophase. The thermal stabilities and mesomorphic temperature ranges of the prepared derivatives are found to be dependent on the length of hydrocarbon chains attached at the ends of the molecule. In addition, the terminal alkenyl chain (in compounds II and III) has a significant effect on the melting temperatures. Binary phase diagrams constructed between two different derivatives I/II and II/D showed low melting temperature, with broad mesomorphic temperature ranges at the eutectic compositions as well as polymorphic phase formation for the II/D system.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/cryst12030350/s1>, S1: Materials; S2: Synthesis of 4-methoxybenzylideneamino) phenol A; S3: Synthesis of Fatty Acid Derivatives, I–III; S4: Characterization.

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