Thermal and Mesomorphic Investigations of 1:1 Supramolecular Assemblies of 4-[(4-(n-Alkoxy)phenylimino)methyl]benzoic Acids Having Symmetrical and Un-Symmetrical Terminal Chain Lengths

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Abstract: Thermal and mesomorphic properties of possible 1:1 supramolecular complexes (SMCs) (I_m/I_n) designed from two members of 4-[(4-(n-alkoxy)phenylimino)methyl]benzoic acid with symmetrical or un-symmetrical alkoxy terminal flexible chains (carbons of m and n = 6, 8 and 16), were analyzed by differential scan-calorimetry (DSC), thermogravemetric (TG) analysis, and their mesophases identified by polarized optical microscopy (POM). The equimolecular mixtures of the two acids possess symmetrical and un-symmetrical terminal lengths. The mesomorphic properties of the binary mixtures were examined as a function of the total alkoxy chain length on both sides. Results revealed that the nematic mesophase temperature range increases as the total terminal length increases for all designed un-symmetrical mixtures. A comparison was constructed between the formed SMCs and of those of the previously prepared 4-n-alkoxyphenylazo benzoic acids as well as the 4-n-alkoxy benzoic acids, to examine the impact of mesogenic core on the mesomorphic properties. The comparison indicated that as the mesogenic portion lengthens the thermal mesophase stability exhibits higher values of phase transition temperatures; whereas, the azo and Schiff base moieties exhibited near thermal properties.

Keywords: symmetrical and un-symmetrical supramolecular-hydrogen bonding; intermolecular interactions; 4-[(4-(n-alkoxy)phenylimino)methyl]benzoic acid; thermal stability; phase transitions

1. Introduction

Supramolecular interactions resulted from H-bonded systems have wide attention in technological applications [1–6]. Liquid crystal (LC) materials have non-covalent interactions as well as potential applications for functional molecular shapes. The shape of the LC compounds depends on the molecular architecture [7–9] and thus has essential role for mesophase formation. One of the most important interactions in biological and chemical processes is the SMC of LCs, namely the association of molecules. Generally, the mesomorphic stability depends on the polarity and/or polarizability of the central mesogenes of the molecule. Numerous of investigated symmetrical and un-symmetrical mesomorphic H-bonding based on the calamitic intermolecular H-bonding interactions [10–15]. Another report has studied the formation of angular complexes through intermolecular H-bond...
formation [16]. Several mesogenic derivatives containing the Schiff base as a central linking group have been reported [17–21].

On the other hand, symmetrical 4-n-alkoxyphenylimino benzoic acids [22] have been shown to possess broad ranges of mesomorphic temperatures compared to their corresponding 4-n-alkoxyphenylazo benzoic acids analogues [15] and simpler acids, 4-n-alkoxybenzoic acids [14]. Other reports have also been interested on the H-bonded LC polymers [23].

The role of H-bonded interaction in the formation and stabilization of LC mesophases has been recognized in recent years [24], its role in the self-assembly of the phase has also been evaluated [25,26]. Thus, the intermolecular H-bond interactions have shown high potential in the thermotropic LC systems [27,28]. In addition, the dimerization of aromatic carboxylic acids is the first example of LC formation [29]. The behaviour of LC material is mainly dependent on the shape of the resulting SMC. Many SMCs are based on the carboxylic and pyridyl components, as proton-acceptor and proton-donor moieties, respectively [30,31].

LC materials for device displays are mostly mixtures because no single compound fulfills all the essential criteria. Therefore, the investigation of mixtures of LC components is a subject of considerable interest [32]. The most used compounds for the preparation of LC blends, via H-bonding interactions, are the benzoic acid derivatives [33]. Thus, the aim of our study is to investigate the possible formation of SMC via H-bonding interactions (I_m/I_n) formed between pairs of 4-n-alkoxyazomethine benzoic acid derivatives having different terminal alkoxy chain length that varies between 6, 8 and 16 carbons. The study also aims to investigate the phase behaviour of the 1:1 molar ratio binary mixtures of any two complimentary components. Furthermore, this study will evaluate the effect of the mesogenic cores as a function of total alkoxy chain length of designed complexes.

2. Experimental

2.1. Synthesis of 4-[(4-(n-Alk oxy)phenylimino)methyl] Benzoic Acid (I_m & I_n)

Materials I_m and I_n were prepared according the previously reported method [22].

2.2. Formation of SM H-Bonded Complexes (I_m/I_n)

Details given in supplementary data (see Scheme 1).
3. Results and Discussion

3.1. Effect of Total Terminal Chain Length on Mesomorphic Behaviours of 1:1 Molar Ratios of SMCs

The possible 1:1 molar binary mixtures that are formed from the three derivatives of 4-n-alkoxyphenylazomethine benzoic acids (Im and In) were prepared. The mesomorphic properties of the prepared mixtures were examined via DSC and POM. The DSC thermograms of Im/I6 homologue are displayed in Figure S3 as a representative example and DSC curves of I6/I8 are depicted in Figure 1. Representative textures of the mesophases under POM are given in Figure 2. For the individual acids as well as their 1:1 molar SMC I6/I16, mesomorphic transition temperatures and their associated enthalpy are summarized in Table 1. Phase transition temperatures, as driven from DSC measurements, are displayed in Figure 3a–c, as a function of the total terminal length (n = m + n) for m and n changed between 6, 8 and 16 carbons, in order to investigate the effect of total terminal alkoxy chain lengths (m + n) on the mesophase behaviour of SMCs. From Table 1 and Figure 3a–c show that an irregular change of melting transitions as the alkoxy chain length increases for all prepared mixtures. Moreover, all SMC showed to exhibit enantiotropic mono- or di-morphic depending on the terminal lengths of chain m and n. The designed supramolecular H-bonding complexes (Im/In) exhibit mesophases of thermal stabilities 262.8, 252.0 and 246.8 °C upon heating for complexes I6/I8, I6/I16 and I8/I16, respectively. Additionally, the stability of the N phase, TN-I, decreases with m; whereas the SmC stability increases with m. For m = 6 (Figure 3a), all SMCs, I6/I8 and I6/I16 including the symmetrical dimer I6/I6 exhibit mesomorphic range about 2.6 °C. These results are in agreement with previous reports [34].

![Scheme 1. Steps of SMCs (Im/In) preparations.](image-url)
that is, the higher difference between the flexible wings of the mixed components, the wide N phase range will observed. For m = 8 (Figure 3b), all SMCs I₈/I₆ have the same trend of I₈/I₆. Moreover, their N stabilities decrease in order to 260.2, 258.0 and 175.8 °C for I₈/I₆, I₈/I₈ and I₈/I₁₆, respectively. In case of the homologues I₁₆/I₈ (Figure 3c), the SMCs I₁₆/I₆ and I₁₆/I₈ show wide nematogenic range nearly 77.3 and 71.0 °C, respectively, while the dimer I₁₆/I₁₆ is purely nematogenic, possessing SmC mesophase with stability temperature 239.7 °C and range 82.7 °C. All results of mesomorphic behaviour revealed that the mixing of one derivative with the other does not disrupt arrangement of molecules within the smectic or N phases.

![DSC thermograms of SMC I₆/I₈](image1.png)

**Figure 1.** DSC thermograms of SMC I₆/I₈ measured at a rate of ±5 °C min⁻¹ from the rounds of second heating and cooling.

![POM textures of mesophases](image2.png)

**Figure 2.** POM textures of mesophases upon heating for SMC I₆/I₁₆ (a) SmC phase at 167.0 °C and (b) N phase at 220.0 °C.

Thermal stabilities of the prepared SMCs, I₆/I₈, also were confirmed by thermogravimetric (TG) analysis (Figure 4). The TGA measurements revealed that, the thermal degradation takes place via one step with the maximum rate loss (Tₘₚ) at ca. 330, 341 and 350 °C for I₆/I₈, I₆/I₁₆ and I₈/I₁₆, respectively. This shows high thermal stabilities for all formed complexes above their isotropic transitions.
Table 1. Mesophase temperatures (°C), enthalpy (kJ/mol) and entropy of transition for the SMCs, I<sub>m</sub>/I<sub>n</sub>.

| System | ñ | T<sub>Cr-SmC</sub> | ΔH<sub>Cr-SmC</sub> | T<sub>SmC-I</sub> | ΔH<sub>SmC-I</sub> | T<sub>SmC-N</sub> | ΔH<sub>SmC-N</sub> | T<sub>N-I</sub> | ΔH<sub>N-I</sub> | ΔS/R |
|--------|---|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------|
| I₆/I₆  | 12 | 189.0            | 55.7             | 257.4            | 2.7              | 265.9            | 1.8              | 0.40             |                  |      |
| I₆/I₈  | 14 | 175.4            | 40.1             | 260.2            | 3.2              | 262.8            | 1.9              | 0.43             |                  |      |
| I₆/I₁₆ | 22 | 158.9            | 39.6             | 174.7            | 2.4              | 252.0            | 1.7              | 0.39             |                  |      |
| I₈/I₈  | 16 | 182.0            | 49.8             | 258.0            | 2.1              | 261.0            | 1.9              | 0.43             |                  |      |
| I₈/I₁₆ | 24 | 158.2            | 36.3             | 175.8            | 2.6              | 246.8            | 1.1              | 0.25             |                  |      |
| I₁₆/I₁₆| 32 | 157.0            | 56.9             | 239.7            | 3.7              |                  |                  |                  |                  | 0.87 |

Abbreviations: Cr-SmC = crystal to smectic C phase; SmC-I = smectic C to isotropic liquid phase; SmC-N = smectic C to nematic phase; N-I = nematic to isotropic liquid phase; ñ = Sum of terminal chain length m + n.

The transition normalized entropy changes (ΔS/R) were estimated for all SMCs and tabulated in Table 1. Dependence of entropy changes with the total length of complexes are represented graphically in Figure 5. From the data in Table 2 and Figure 5, the entropy changes (ΔS/R) showed slight decrement values with the increase of the total alkoxy chain length ñ up to ñ = 24 carbons (ΔS/R =0.25) then jump to (ΔS/R = 0.87) at ñ = 32. The specific interactions between the un-like mesogens leads to the production of the smectic mesophase in un-symmetric complexes [35,36]. The irregular relation may be attributed to the different type of mesophases of complexes from ñ = 12 to ñ = 24. ΔS/R of ñ = 24 is lower than that of ñ = 22 which may be attributed to the different biaxiality of their mesogenic groups arrangement [37,38]. The N mesophases covered all of the SMC mixtures, while for ñ = 32 only the SmC mesophase was observed. Thus, the increase of the end–to-end associations of molecules with increasing the total length of the molecule is a result of the production of wide range of N phase up to ñ = 24. Additionally, the relatively small values...
Dependence of the entropy changes (Figure 5).

The values of $\Delta S/R$ for LC cholesteryl complexes bearing –S–S– link were found to be little which may be due to the increment of biaxiality of molecules which arising from the dihedral angle of C–S–S–C.

Figure 4. TGA plot of SMC $I_6/I_8$, as an example, recorded at heating rate of 10 °C min$^{-1}$ under nitrogen.

Figure 5. Dependence of the entropy changes ($\Delta S/R$) on the total alkoxy chain length (n) of SMCs, $I_m/I_n$. 
3.2. Effect of Mesogenic Cores on the Mesophase Stability of SMCs

The terminal flexible length and the mesogenic portion of components have effective roles on the thermal stability and the type of the formed mesophase. It had been documented that the difference polarity between H-acceptor and H-donors impacts the strength of H-bonding and lengthen the molecular anisotropy as well as broaden of the mesomorphic range [15]. On the other side, the polarity of either components of the mixture is not impacted by the length of the ends group. In order to evaluate the effect of different mesogenic cores on the mesomorphic stability ($T_C$), comparisons were made between the present SMCs, $I_m/I_n$, and the our previously investigated 4-n-alkoxy phenylazo benzoic acids complexes, $II_m/II_n$ [15] and simple 4-alkoxybenzoic acids mixtures ($III_m/III_n$) [14]. Thermal stabilities ($T_C$) data for all SMCs are collected in Table 2 and displayed graphically in Figure 6. The comparison was established between their mesomorphic stabilities ($T_C$) as a function of total alkoxy chain length ($n$). The comparison of $I_m/I_n$ with the simplest complexes $III_m/III_n$ revealed that, the incorporation of extra Schiff base linkage has led to increment the mesogenic core length and consequently, the mesomorphic thermal stability of present investigated mixtures show higher values of transition temperatures.

Another comparison was established between the phase stability of Schiff base complexes ($I_m/I_n$) and their corresponding phenylazo benzoic acids mixtures ($II_m/II_n$) and the data indicated that, both series having near thermal stabilities after replacing the –N=N-linkage by –N=CH- covering all total alkoxy chain lengths ($n$) except for $n = 22$ and $24$ the azomethine complexes ($I_m/I_n$) which showed to possess higher thermal mesophase stabilities than those of the azo based mixtures ($II_m/II_n$). These results indicate that the Schiff base and azo moieties exhibit nearly the same polarizability values. On the other hand, the previous study of the phenylazo mixtures [15] revealed that, as the mesogenic core length is increased the phase stabilities of smectic and N phases are increased. In addition, the mesomorphic range of SmC formed has shown to also be increased upon the incorporation of the phenylazo unit. While in the present investigated Schiff base mixtures ($I_m/I_n$) the stability of SmC slightly decreases as the length of tails become increases which may be attributed to participation of other geometrical parameters that affects the molecular arrangements. Moreover, their SmC and N ranges have shown to change in irregular manners.

![Image of molecular structures](image-url)
Table 2. Thermal mesophase stabilities of systems $I_n/I_n$, $II_n/II_n$ and $III_m/III_n$.

| $\bar{n}$ | System $-N=CH-$ | $T_C$ | System $-N=N-$ | $T_C$ | System $-N=N-$ | $T_C$ |
|-----------|----------------|------|----------------|------|----------------|------|
| 12        | $I_6/I_6$      | 265.9| $II_6/II_6$    | 264.0| $III_6/III_6$  | 158.0|
| 14        | $I_8/I_8$      | 262.8| $II_8/II_8$    | 266.0| $III_8/III_8$  | 151.6|
| 16        | $I_8/I_8$      | 261.0| $II_8/II_8$    | 260.0| $III_8/III_8$  | 147.0|
| 22        | $I_{16}/I_{16}$| 252.0| $II_{16}/II_{16}$| 241.0| $III_{16}/III_{16}$| 130.2|
| 24        | $I_{16}/I_{16}$| 246.8| $II_{16}/II_{16}$| 242.9| $III_{16}/III_{16}$| 133.0|
| 32        | $I_{16}/I_{16}$| 239.7| $II_{16}/II_{16}$| 240.0| $III_{16}/III_{16}$| 132.5|

Figure 6. Dependence of thermal mesophase stabilities of the complexes $I_m/I_n$, $II_m/II_n$ and $III_m/III_n$ on the total terminal alkoxy chains length.

4. Conclusions

New binary series of 1:1 molar SMC of 4-[(4-(n-alkoxy)phenylimino)methyl]benzoic acids, with symmetrical and un-symmetrical proportionated terminal alkoxy chain lengths, were prepared and investigated thermally and mesomorphically. The results revealed that all mixtures are dimorphic with enantiotropic SmC and N phases. With a Lengthening of the total alkoxy chain, in the two wings of the 1:1 SMCs, the N phase temperature range increases. In addition to all designed SMCs show high thermal stability above their isotropic temperatures. The comparison between the present SMCs ($I_m/I_n$) and each of the previously investigated 4-n-alkoxyphenylazo benzoic acids complexes ($II_m/II_n$) and its simpler analogues ($III_m/III_n$) revealed that increasing the mesogenic core length is associated with a considerable conjugative interactions between the terminals of each of the two components in binary mixtures that show parallel phase behaviour as a function of the total alkoxy chain lengths. Moreover, the effect of the alkoxy chain length that is...
attached to the ring of the azomethine moiety is found to be more effective compared with those connected to benzoate unit which is nearly similar to the phenylazo analogues.

Supplementary Materials: The following are available at https://www.mdpi.com/article/10.3390/sym13101785/s1. The synthetic and characterization details of investigated compounds as well as Figures S1–S4.

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