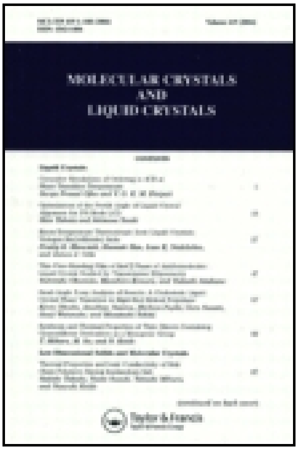

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# Thermotropic-like Character and Vesicular Aggregation of N, N′ Didodecyl Succinamic and Maleamic Acids†

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In the present study the synthesis is reported of two novel compounds, i.e. N,N′ didodecyl succinamic and maleamic acids, that exhibit thermotropic-like properties and form vesicles in aqueous media. Thermotropic character, which was shown by optical and differential scanning calorimetric studies, was attributed to a lamellar structure whose thickness must be equal to the length of the dimers formed through hydrogen bonding between the carboxylic groups of the compounds. Vesicle formation was established by electron microscopy and rationalized with the structure of the molecules which have a characteristic double long chain lipophilic portion coupled to a polar group.

## INTRODUCTION

A survey of liquid crystal literature reveals that thermotropic mesomorphism is not an exclusive property of long planar rigid molecules i.e. of compounds bearing typical mesogenic moieties coupled with appropriate functional groups. In this connection it has been found that phospholipids[1] with two long alkyl chains show thermotropic liquid crystalline behavior in addition to their common property of

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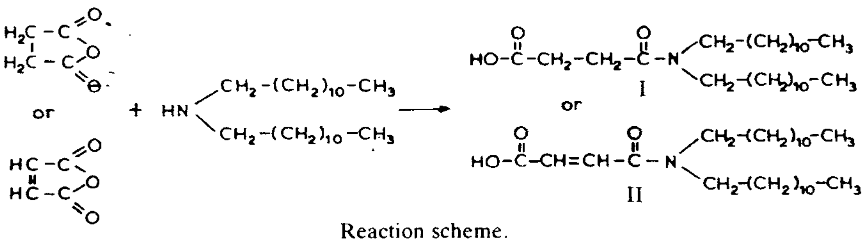
aggregation in aqueous media to form bilayer structures and/or vesicles. In addition it has been established by Kunitake[2-4] that certain conventional mesogenic moieties when functionalized with strong polar heads (i.e. quaternary ammonium or phosphate groups) not only exhibit thermotropic behavior but also form bilayers in water. Furthermore, Vocatello and coworkers[5-8] and quite recently, Willet et al[9] investigated the thermal behavior of certain primary alkylammonium salts and established the existence of a lamellar smectic mesophase. Further Iwamoto et al,[10] in studying the thermal transitions of some long-chain n-alkyltrimethylammonium halides, showed that their solid-solid transition leads to "mesophases" or mesomorphic-like phases since completely free motion of the quaternary salts is not allowed due to the ionic bonding between the quaternaries and halide ions. We have also observed the same behaviour with certain long chain functionalized quaternary ammonium salts. These not only show thermotropic-like behaviour[11] but also form micelles[12] in water. Therefore it is clear that there must be a relationship between the ability of molecules to organize by aggregation in water and thermotropic liquid crystallinity. In this context *N,N′* didodecyl succinamic acid (**I**) and *N,N′* didodecyl maleamic acid (**II**), resulting from the reaction of succinic or maleic anhydride with didodecylamine and possessing both lipophilic and hydrophilic segments, may in principle exhibit thermotropic and/or lyotropic mesomorphism. Our first results are discussed in this paper.



Reaction scheme.

## EXPERIMENTAL

*Didodecylamine*: This was prepared by the reaction of dodecylamine with Raney nickel as described by Ralston et al.[13]

*Synthesis of* **I**: Succinic anhydride, 0.01 mole, was dissolved in dry alcohol free chloroform. Then 0.01 mole of didodecylamine was added to this solution and the mixture was left under stirring, for several hours at room temperature. The solvent was distilled off and the oily material was crystallized from ethyl alcohol and recrystallized from the same solvent.

Calculated Analysis for $C_{28}H_{55}O_3N$: C, 74.18%; H, 12.13%, N, 3.08%.
Observed Analysis: C, 74.01%; H, 12.42%; N, 3.18%.

*Synthesis of* **II**: The same procedure employed for the synthesis of I was used for the preparation of II.

Calculated Analysis for $C_{28}H_{53}O_3N$: C, 74.51%; H, 11.74%, N, 3.10%.
Observed Analysis: C, 74.78%; H, 11.69%; N, 3.14%.

Optical microscopy was carried out using a Reichert "Thermopan" polarizing microscope and thermal studies were performed with a Dupont 910 Differential Scanning Calorimeter at a scanning rate of 10°C/min. Cooling was at the module's natural rate.

Vesicles of **I** and **II** were formed by sonicating their 0.01 M dispersions at a pH = 9 (borate/hydrochloric acid) using a MSE probe sonicator at a level 6 to 6, 5 for 45 min. The resulting vesicles were freed of titanium particles and other big aggregates by filtration through a 0.45 nm filter. The filtrate was applied on carbon-coated grids

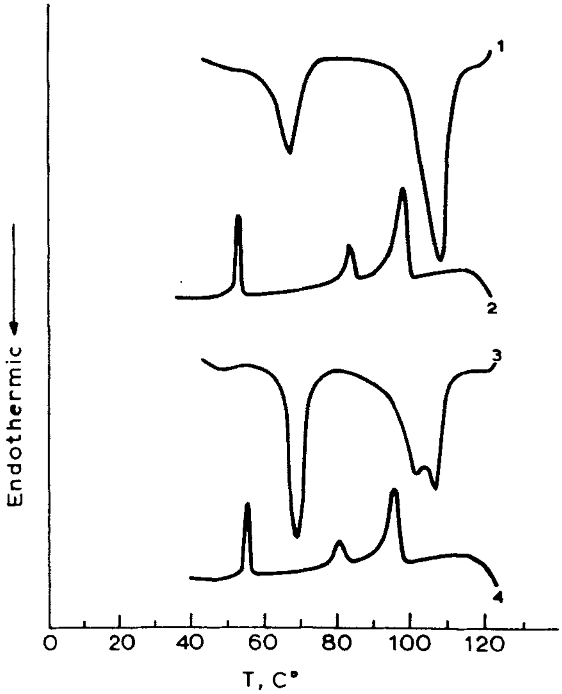
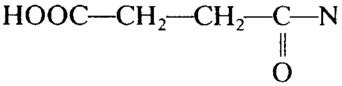


FIGURE 1 DSC curves of compound **I**. 1. First heating, 2. First cooling, 3. Second heating, 4. Second cooling.

occasionally stained with 2% uranyl acetate and subsequently examined with a Philips EM 200 electron microscope operating at 60KV.

## RESULTS AND DISCUSSION

The simultaneous introduction of a lipophilic portion (consisting of two alkyl chains and a hydrophilic carboxylic head) in compounds **I** and **II**, was accomplished under very mild experimental conditions employing a well-known reaction.[14] The hydrophilic head may be considered to include not only the carboxylic group but also extend to the amide nitrogen (i.e.  $HOOC{-}CH_2{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}N$ for I and

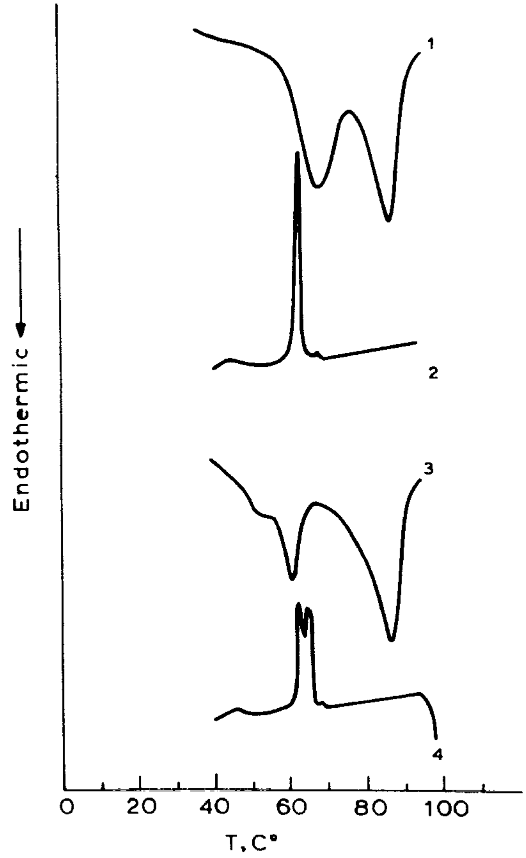
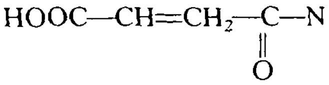


FIGURE 2 DSC curves of compound **II**. 1. First heating, 2. First cooling, 3. Second heating, 4. Second cooling.



$HOOC{-}CH{=}CH_2{-}\underset{\underset{O}{\|}}{C}{-}N$ for II) and the presence of the ethylenic group is considered as responsible for the difference in the properties of the compounds in question. A first difference is the difficulty experienced in crystallizing compound **II** as several days, at approximately −10°C, are required for its crystallization or recrystallization in contrast to the fast crystallization of **I**.

Compounds **I** and **II** exhibited multiple step melting behaviour as

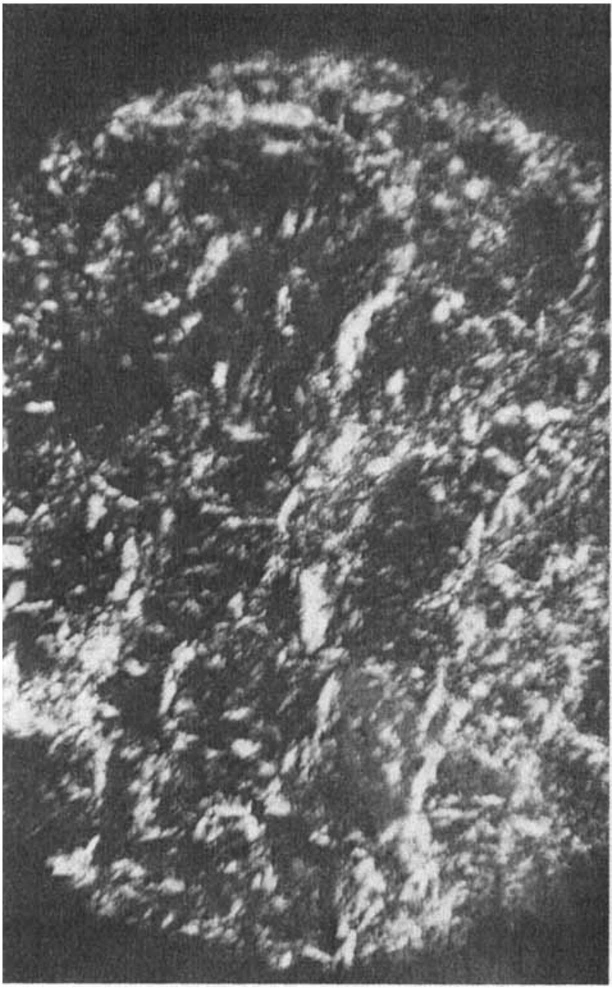


FIGURE 3 Photomicrograph of sample **I** under crossed polarizers (heating cycle).

established by differential scanning calorimetry. The thermograms of **I** and **II** for two heating/cooling runs are shown in Figures 1 and 2. On cooling from the isotropic melt substantial supercooling occurs for compound **II** as is evident from Figure 2. However both compounds exhibited satisfactory thermal stability, as shown by the consistency of the final transition manifest during three heating runs (this third transition is not shown in the figures).

This multiple melting behavior was also observed on heating **I** and

FIGURE 4 Photomicrograph of sample **II** under crossed polarizers (heating cycle).

**II** on a hot stage of a polarizing microscope. When pressure was exerted on the cover-slip, at temperatures always exceeding the first transition, both compounds showed anisotropic melt behavior under crossed polarizers. The same phenomena were observed without pressing the cover-slips, the transitions however were shifted to higher temperatures. As shown in Figures 3 and 4, partially homoetropic textures were obtained for **I** and **II** which were transformed to isotropic melts at 114°C and 85°C respectively. On cooling from the isotropic phase **I** crystallizes at the mesomorphic-isotropic transition temperature, while **II** exhibits substantial supercooling. Polymorphic modifications obtained after melting to the isotropic phase were difficult to deform both during cooling and heating runs. We may attribute the thermotropic or rather thermotropic-like character of these compounds to the tendency of their molten long aliphatic chains, in conjunction with their polar heads, to maintain a lamellar structure in analogy to that proposed for ionic amphiphiles and discussed above. In this case however instead of ionic bonding between quaternaries and halide ions, we may envisage hydrogen bonding between carboxylic groups resulting in the formation of dimers, in a way analogous to conventional liquid crystalline molecules that bear carboxylic groups.[15] In the mesomorphic phase the thickness of the lamellae is

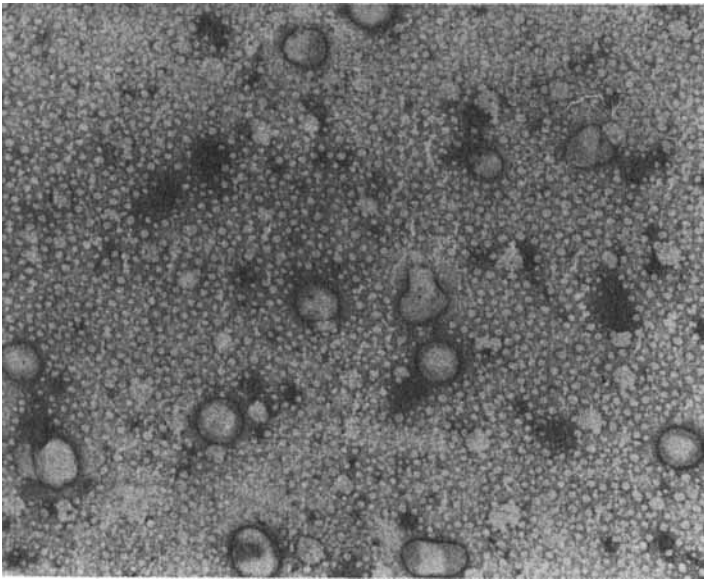


FIGURE 5 Electron micrograph of **I** (Magnification X 16,000).

equal to the length of the dimers, and lamellae can slide with respect to each other since the terminal van der Waals bonding between nonpolar layers has been broken. Mesomorphic-isotropic transitions would then have to be related to the dissociation of the dimers to monomeric acids.

In alkaline media compounds **I** and **II** are primarily anions which, with sonication, form vesicles as shown in Figures 5 and 6. Vesicles resulting from **I** are unstable and on standing for several hours they form a gel-like material. Vesicles resulting from the sonication of **II** are stable and remain in the vesicular phase for long periods of time (more than a month) although turbidity soon appears. It is interesting to note, however, that the introduction of the double bond (compound **II**) significantly affects the stability of its vesicles and is attributed to the enhancement of the polar character of hydrophilic segment.

In conclusion, the interaction of certain cyclic anhydrides, such as

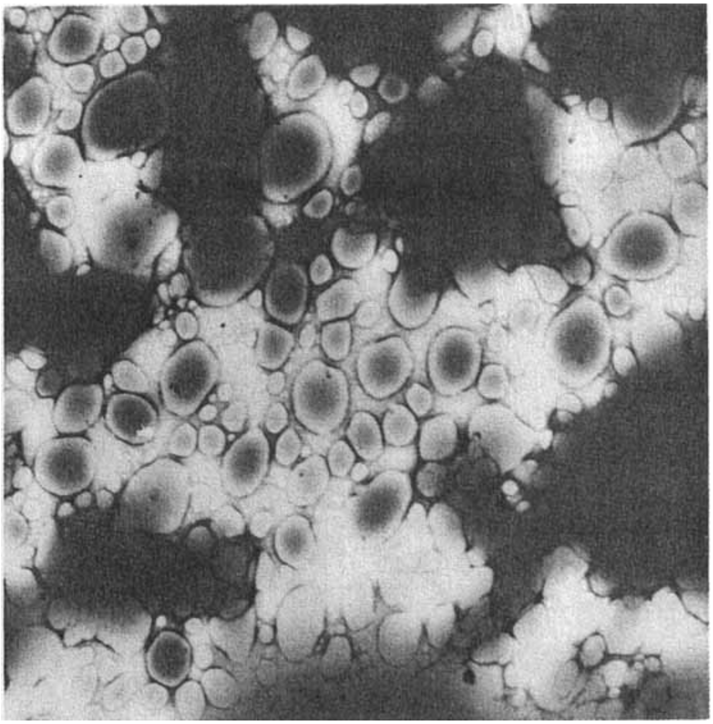


FIGURE 6 Electron micrograph of **II** stained with 2% uranyl acetate (Magnification X 27,300).

succinic and maleic anhydrides with didodecylamine, results in the preparation of the amphiphilic compounds **I** and **II** that exhibit thermotropic-like behavior and aggregate as vesicles in water. Finally further characterization of this so-called thermotropic-like phase may be carried out by x-ray scattering studies and there will be performed in the near future.

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