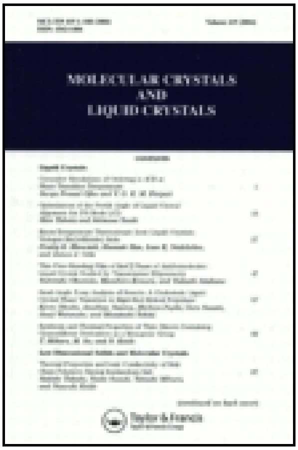

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A New Family of Liquid Crystals: N Substituted Aldonamides I. Thermotropic Behaviour of N-Decylribonamide

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A New Family of Liquid Crystals: *N* Substituted Aldonamides. I. Thermotropic Behaviour of *N*-Decylribonamide

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Neat *N*-decylribonamide forms a lamellar mesomorphic phase between 99°C and 151°C. This phase has been identified and characterized by DSC and by examination of the textures with the polarizing microscope. A probable arrangement of the molecules in the lamellae is proposed and discussed.

1. INTRODUCTION

The solvent-induced mesophases of amphiphilic mesogens have been extensively investigated. Their thermotropic behaviour is however far less well known than that of non-amphiphilic mesogens. Several anionic amphiphiles form mesophases which organize as a function of temperature when in the neat (i.e., anhydrous) condition.[1] A few non-ionic amphiphiles have been reported to yield mesophases when in the neat fused state. Examples are given by the shorter chain 2-monoglycerides which yield lamellar liquid crystals on cooling from the amorphous melt and by n-alkylglucosides.[2]

This paper reports the thermal behaviour in the neat phase of *N*-decylribonamide (I) which is a member of a family of non-ionic amphiphilic mesogens which has not been previously described. Many *N*-substituted amides of aldonic acids exhibit not only lyotropic mesomorphism, but also thermotropic mesomorphism of the neat phase. The relation between their chemical structure and their thermotropic behaviour in the neat phase will be published soon.

TABLE I

NMR identification of *N*-decylribonamide $(C_{15}H_{31}O_5N_O)$

A. ^{13}C NMR (63 MHz)	DMS0 (δ_{dmso} ppm)	
δ_{ppm}	multiplicity[a]	assignment
133.0	C	C = O
34.6	CH	CHOH
33.4	CH	CHOH
32.8	CH	CHOH
23.9	CH_2	CH_2OH
− 1.0	CH_2	CH_2N
− 8.0	CH_2	
− 10.2	CH_2	
− 10.3	CH_2	8 CH_2
− 10.3	CH_2	
− 10.5	CH_2	
− 10.6	CH_2	
− 12.9	CH_2	
− 17.2	CH_2	
− 25.4	CH_3	CH_3

B. ^1H NMR (250 MHz)	DMSO (δ_{dmso} ppm)		
δ_{ppm} → aligned	multiplicity	J (Hz)	assignment
5.05 (1H)	tr	6	NH
2.95 (1H)	d	6	CH O*H*
2.22 (1H)	d	5	CH O*H*
2.01 (1H)	d	5	CH O*H*
1.81 (1H)	tr	5	CH_2OH
1.51 to 0.88 (5H)	m	—	3C*H*OH + CH_2OH
0.81 (1/2H)	s	—	H_2O
0.56 (2H)	q	6.5	CH_2N
− 1.26 (16H)	s	—	$(CH_2)_8$
− 1.64 (3H)	tr	7	CH_3

[a] determined by using the DEBT pulse sequence

2. SYNTHESIS AND CHARACTERIZATION

D(+)-γ-ribonolactone (1.0 g) is dissolved in 5 ml methanol. *N*-decylamine (1.1 g) is then added to the solution and the whole allowed to react at room temperature for 3 h.[3] The crude product is recrystallized three times from ethyl acetate. Under these conditions, the *N*-decylribonamide crystallizes with two water molecules as determined by ^{1}H NMR (Table I) using a Bruker WM 250 apparatus. A further purification designed to obtain anhydrous amide is then performed. The crystallized amide is suspended in benzene and heated under reflux for two hours to eliminate the benzene-water azeotrope. After filtration, the residual benzene is eliminated under vacuum. The water content of the amide is then reduced to 0.25 water molecule per amide molecule.

The ^{13}C and ^{1}H NMR (Table I) spectra confirm structure I for the amide formed.

3. THERMAL BEHAVIOUR

3.1. Differential scanning calorimetry

Differential scanning calorimetry performed with Perkin-Elmer apparatus DSC 2 (10°C. min^{-1}) reveals the presence of two phase transitions observed at 99°C and 151°C on heating the sample. The ΔH are respectively 16.24 and 0.39 kcal mole^{-1}. On cooling, the latter transition is observed at 147°C, while the former exhibits a very pronounced supercooling and is observed at 62°C. The transition temperatures, ΔH values, and textures are identical whether the number of water molecules per mole of amide is 0.25 or 2.

3.2. Microscopic identification of the textures

The textures observed between crossed polars are in complete agreement with those described by Rosevear[4] for the lamellar phase of sodium and potassium soaps in aqueous solution†. Homeotropic areas

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† For clarity's sake, the terms "lamellar phase" and "rodlike hexagonal phase" will be used in the present work. The lamellar phase corresponds to the neat phase of Rosevear[4] and to the G phase used by Gray and Winsor.[5] The nomenclature L_α, L_β.. proposed by Luzzati[6] needs further details of the arrangement of the molecules in the lamellae to be given. The rodlike phase corresponds to Rosevear's middle phase[4] and to Gray and Winsor's *M* phases.[5]

areas corresponding to uniaxial planar textures appear after the first transition, either spontaneously or induced by a small motion of the cover glass (Fig. 1). These planar areas contain circular spherulites with positive optical sign which correspond, according to Rosevear, to "unit" focal conic textures. Each positive unit constitutes a focal domain viewed normal to its elliptical base. In this special case, the ellipse is a circle and the hyperbola is a straight line normal to the circular base. Rosevear's "negative units", resulting from the fact that the vertices of adjacent positive units are alternately on the top and bottom surfaces of the preparation, are also observed. Vigorous movement of the cover glass transforms the planar areas into mosaic regions (Fig. 2) which are not observed in the rodlike hexagonal phase and are characteristic of the lamellar phase. Another focal-conic texture frequently observed in lamellar phases consists of oily streaks formed on the border of planar areas (Fig. 3). Also "*bâtonnets*" precipitate on rapid cooling from the isotropic phase. All the textures reported by Rosevear[4] for the lamellar phase have thus been observed in the case of neat *N*-decylribonamide, whereas none of the geometric textures reported for the rodlike phase could be

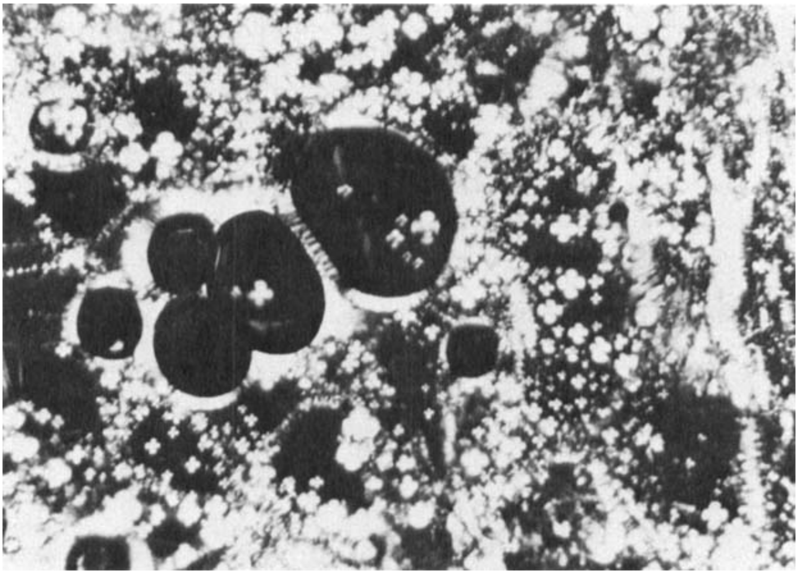

FIGURE 1 *N*-Decylribonamide observed at 100°C between crossed polarizers: Planar textures—spherulites with positive optical sign.

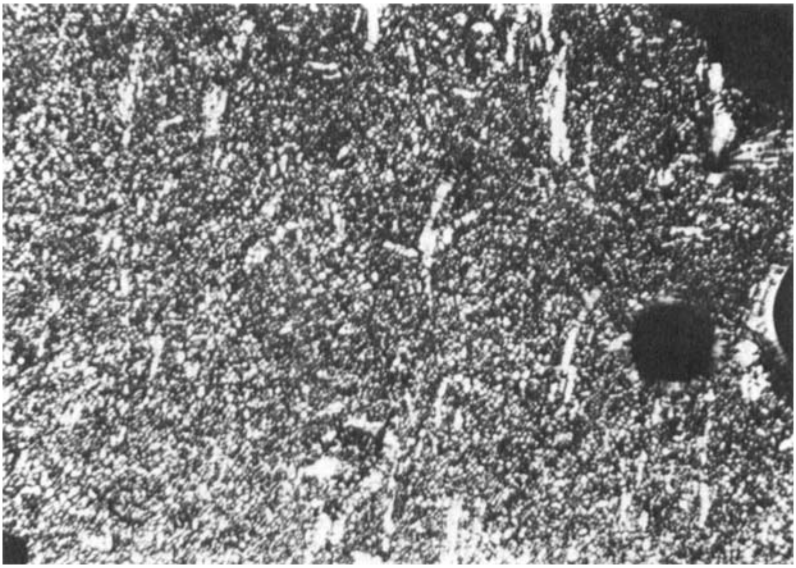

FIGURE 2 *N*-Decylribonamide observed at 126°C after vigorous movement of the cover glass: mosaic texture.

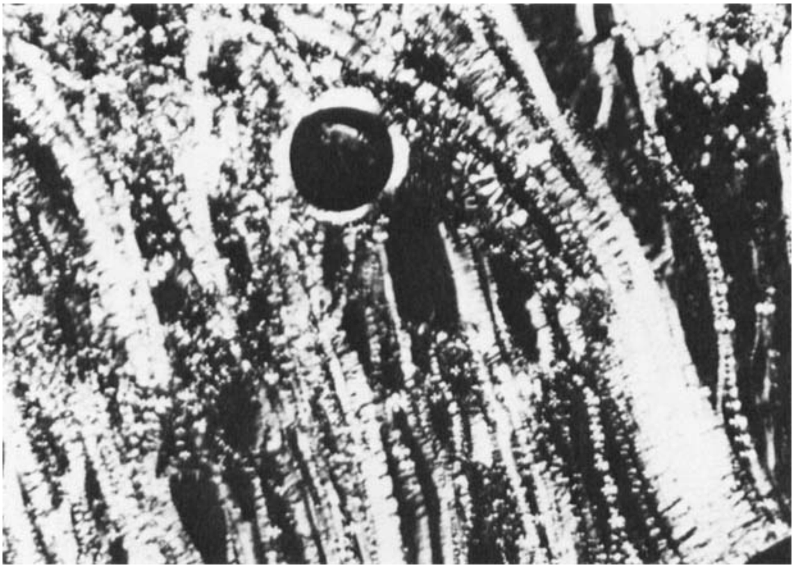

FIGURE 3 *N*-Decylribonamide: oily streaks observed at 124°C.

detected.† We thus identify the mesophase formed by this ribonamide between 99 and 151°C as lamellar. Confirmation of the lamellar structure and determination of the conformation of the paraffinic chains by X-ray diffraction would have been of interest. However, the thermal stability of the amide in the neat mesomorphic state is not sufficient to allow such an identification. Study of the crystal structure can yield important information about hydrogen bonding and hydrocarbon chain packing as observed for *n*-alkylglucosides.[7] This work is now in progress.

4. DISCUSSION

The DSC measurements and the examination of the textures observed with the polarizing microscope have shown that a lamellar organization is present in neat *N*-decylribonamide between 99 and 151°C. The 'residual' water molecules do not appear to modify the nature of the mesophase or the temperature of transition. These observations are in agreement with previous observations reported in the literature. Although mesophases corresponding to the lamellar and "rodlike hexagonal" arrangement of the molecules have been reported for solutions of amphiphiles, the lamellar one has been most often identified in the absence of water.[1]

The arrangement of molecules in the lamellae needs further discussion. Amides are known to exist as two configurational isomers, *cis* (II) or *trans* (III), arising from the lack of free rotation about the C(O)-N bond.[8] The *trans*-isomer has been shown by NMR to predominate for *N*-alkylamides in solution.[9] The *trans*-isomer would be still favoured in the present case by H-bonding between the amide-NH and the OH of the ribonic residue (IV). Two possible associations can arise for the least probable *cis*-isomer and the most probable *trans*-isomer. They are respectively the H-bonded dimer V and the H-bonded polymer VI which have been observed in concentrated solutions. Formation of the lamellae could arise either by assembling

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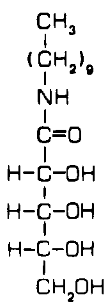
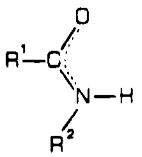
†If a "rodlike hexagonal" middle phase organization occured in the neat amide phase, it would probably be a M_2 mesophase in which the polar groups constitute the core of the micelles. The middle phase textures reported by Rosevear concern M_1 mesophases formed in the presence of water where the polar groups of the amphiphile lie at the outside of the cylindrical micellar aggregates. Textures of the M_2 phase as observed microscopically have however been reported to be analogous to those of the M_1 phase.[5]



I



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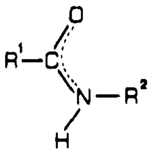
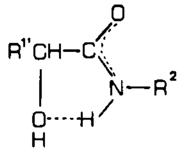
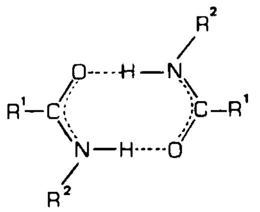


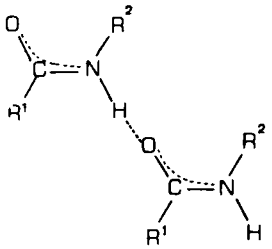
III



IV



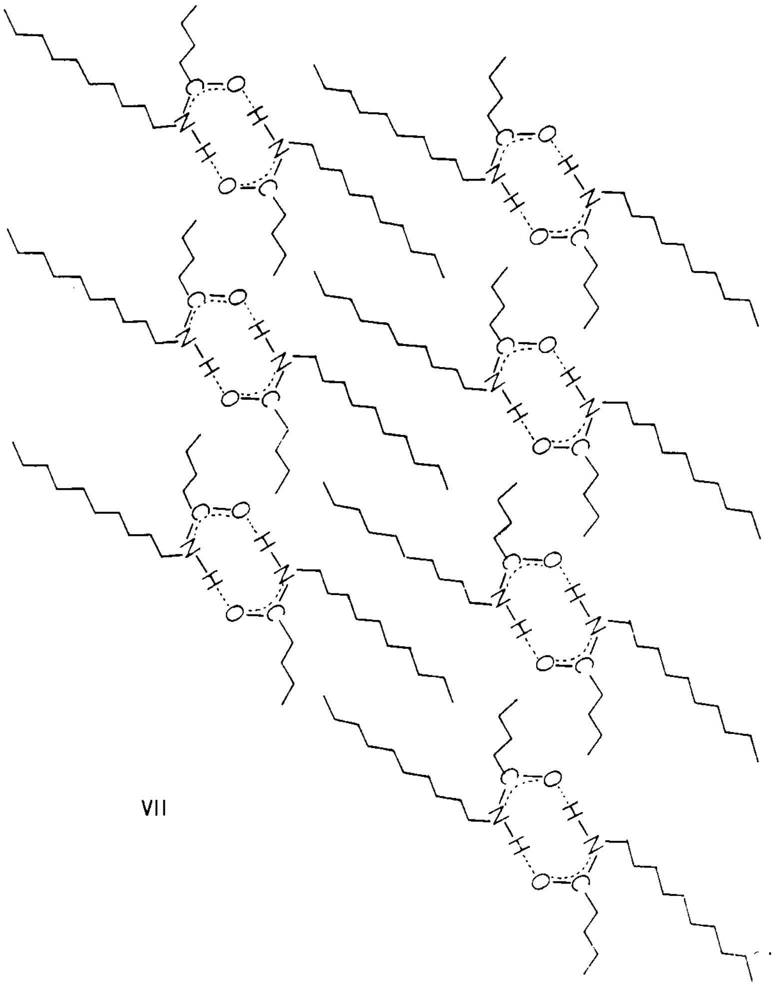
V



VI

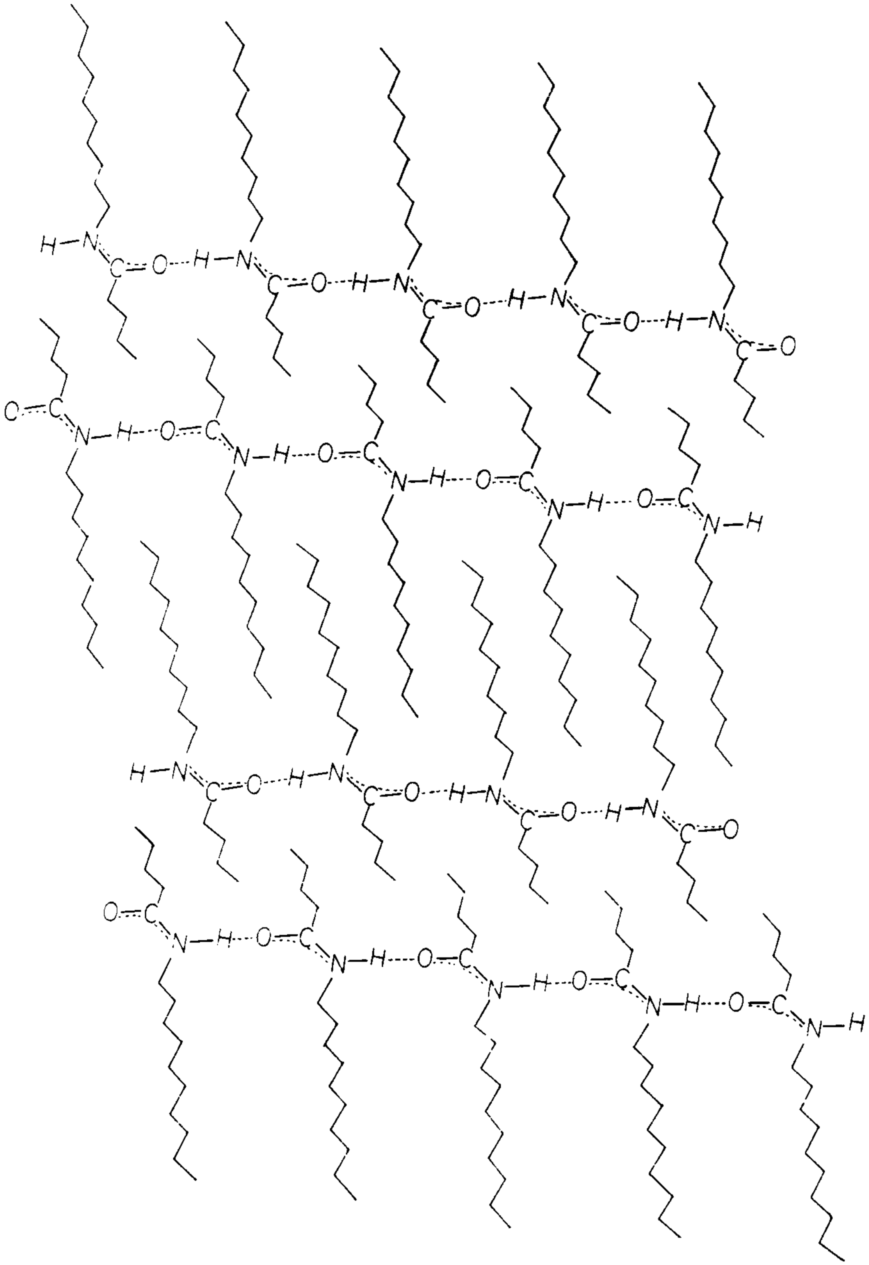
cis-dimers V according to structure VII, or by assembling *trans*-polymers as in VIII. Hydrophobic interactions and H-bonding between respectively R^2 and R^1 chains of neighbouring stacked dimers would have a stabilizing influence. Arrangement VII is however less probable and would be less stable than lamellae formed from the H-bonded polymer VI and represented by structure VIII. Hydrophobic interactions between R^2 chains and H-bonding interactions between R^1 chains are also operating in this last case, in addition to H-bonding between amide bonds. Complete separation of the hydrophobic R^2 chains and hydrophilic R^1 chains would however favour VIII when compared to VII. We thus propose structure VIII for the arrangement of molecules in the lamellar mesophase of *N*-decylribonamide.

Further information about the nature of the interactions between



VII

the molecules and the probable formation of bilayers by interdigitation of the hydrocarbon chains will be afforded by the systematic study of mesophase formation in a large number of compounds differing by the nature of the alkyl and hydrophilic chains and by the nature of the functional group linking them. This study is now being completed.[10] X-ray studies of the molecular packing in the crystal are in progress.



VIII

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