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A New Family of Liquid Crystals: N-Substituted Aldonamides II: Relationship Between Chemical Structure and the Formation of Mesophases

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A New Family of Liquid Crystals: N-Substituted Aldonamides
II: Relationship Between Chemical Structure and the Formation of Mesophases

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A series of N-substituted aldonamides has been synthesized. Some of these compounds form a thermotropic lamellar mesophase in which molecules in the *trans*-configuration are arranged in monolayers stabilized by hydrogen bonding and hydrophobic interactions. X-ray diffraction studies have shown that a molecular arrangement of this type exists in the crystalline solid of N-decylribonamide. The relationship between the mesogenic properties and the molecular structures of these compounds is discussed (with reference to the length, branching and cyclisation of the aldonic residue and of the hydrocarbon chain).

Keywords: N-aldonamides, lamellar thermotropic phase, crystal structure determination

INTRODUCTION

The thermotropic behaviour of amphiphilic mesogens is far less well known than that of non-amphiphilic compounds. Several ionic amphiphiles, mainly salts of fatty acids[1,2] give mesophases when heated in the neat state but examples of thermotropic *non-ionic* amphiphiles are rare.

Neat N-decylribonamide has been recently reported as forming a lamellar mesophase between 99 and 151°C.[3] This compound is a member of a family of non-ionic amphiphilic mesogens which has not been previously described. The present work is a systematic investigation of the relationship between the chemical structure and mesogenic properties for a broad range of aldonamides. The structural features studied are the length, branching and cyclization of both the aldonic residue and of the hydrocarbon chain, the presence of phenyl groups in the hydrocarbon chain and the nature of the functional groups between the aldonic residue and the hydrocarbon chain.

EXPERIMENTAL

The amines were added in stoichiometric proportion to the aldonic acid or to the aldonolactone dissolved in methanol. The different starting materials, the reaction time and the crystallization conditions are given in Table I. The reaction temperature was 20°C unless otherwise specified. The products obtained were characterized by their transition temperature, the frequency of the amide I absorption in the IR and their ^{13}C NMR spectra (Table II and III). The NMR and IR spectra confirmed the structures given in Table II.

The ester was prepared using acetonitrile as solvent. The solid obtained was dissolved in ether and filtered at 35°C.

Transition temperatures were recorded and the textures identified with a Laboval (Zeiss) polarizing microscope equiped with a Mettler FP52 hot stage using a heating rate of 3°C/min.

Differential scanning calorimetry was carried out with a Perkin-Elmer DSC 2 (10°C/min).

The IR spectra were recorded with a Perkin-Elmer 257 grating Infra-red spectrophotometer. The sample was dispersed in KBr pellets. The effect of temperature on the amide I vibration of isosaccharinamide was kindly studied by Dr Zichy from ICI (Welwyn Garden).

The ^{13}C NMR spectra were recorded, in solution in DMSO, using a 63 MHz Bruker apparatus. The multiplicity was determined using DEBT pulse sequence.

CHARACTERIZATION OF THE AMIDES

NMR spectra of solutions

The ^{13}C and ^{1}H spectra of N-decylribonamide are given in reference 3. The shifts of the hydrocarbon chain of the amides reported in the

TABLE I

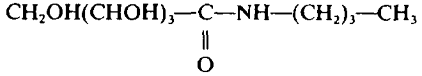
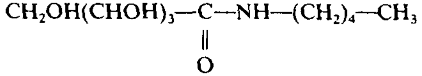
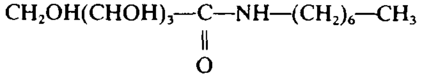
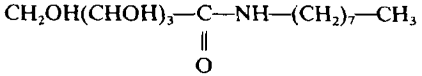
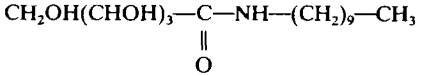
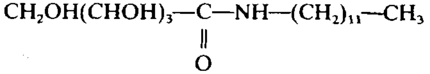
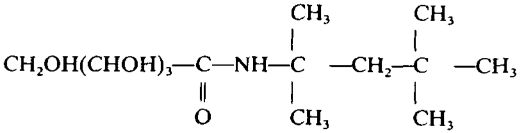
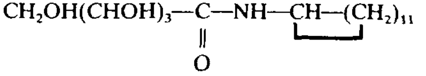
Synthesis and purification of substituted aldonamides

Acid	Amine	Product	React. time under[a] N_2(h)	Crystallization solvent
D(+)-ribonic acid-γ-lactone	n-butylamine	I	15	CH_3CN (3x)
	n-amylamine	II	12	CH_3CN (3x)
	n-heptylamine	III	3-4	CH_3CN (3x)
	n-octylamine	IV	24	MeOH (2x)
	n-decylamine	V	3	Ethyl Acetate (3x)
	n-dodecylamine	VI	3-4	MeOH (2x)
	t-octylamine	VII		CH_3CN (3x)-MeOH (1x)
	cyclododecylamine	VIII	3^b	CH_3CN (3x)-MeOH (1x)
	phenetylamine	IX	12	CH_3CN (2x)
	p-phenylbutylamine	X	3	MeOH (2x)-CH_3CN (1x)
	p-butylaniline	XI	3^c	Ether (1x)-EtOH (1x)
	p-anisidine	XII	1^d	CH_3OH (2x)-CH_3CN (1x)
	p-benzoxyphenetylamine	XIII	120	CH_3CN (2x)
	p-hexoylphenetylamine	XIV	72	CH_3CN (2x)
D-glucuronic acid-γ-lactone	n-decylamine	XV	20	MeOH (3x)-CH_3CN (2x)
gluconic acid	n-octylamine	XVI	4	MeOH (3x)
	n-decylamine	XVII	4	MeOH (3x)-CH_3CN (1x)
	n-dodecylamine	XVIII	4	MeOH (3x)-CH_3CN (1x)
α-D-glucoheptonic acid-γ-lactone	n-decylamine	XIX	2-3	MeOH (3x)
isosaccharinic acid-γ-lactone	n-decylamine	XX	72	Ethyl Acetate (2x)-H_2O (1x)
	n-dodecylamine	XXI	72	CH_3CN (3x)
	n-hexadecylamine	XXII	72	CH_3CN (3x)
gluconic acid	n-decyl alcohol	XXIII	6^e	H_2O

[a] The reaction was performed at room temperature unless otherwise specified.
Reaction temperature: [b] 30°C, [c] 98°C, [d] 100°C, [e] 90°C.

TABLE II

Transition temperatures [a] and frequency of the amide I band for substituted aldonamides

Aldonamide		Crystalline compounds $T_{C\to I}$ °C	Liquid crystalline compounds $T_{C\to L}$ °C	$T_{L\to I}$ °C	ν C=O cm^{-1} [c]
I	 $CH_2OH(CHOH)_3-\underset{\underset{O}{\|}}{C}-NH-(CH_2)_3-CH_3$	88			
II	 $CH_2OH(CHOH)_3-\underset{\underset{O}{\|}}{C}-NH-(CH_2)_4-CH_3$	98.5			
III	 $CH_2OH(CHOH)_3-\underset{\underset{O}{\|}}{C}-NH-(CH_2)_6-CH_3$		94	95 (96)[a]	1655 (1620)
IV	 $CH_2OH(CHOH)_3-\underset{\underset{O}{\|}}{C}-NH-(CH_2)_7-CH_3$		96 (97)	120 (123)	1655 (1620)
V	 $CH_2OH(CHOH)_3-\underset{\underset{O}{\|}}{C}-NH-(CH_2)_9-CH_3$		100 (99)	147 (151)	1655 (1620)
VI	 $CH_2OH(CHOH)_3-\underset{\underset{O}{\|}}{C}-NH-(CH_2)_{11}-CH_3$		106 (105)	158 (160)	1660
VII	 $CH_2OH(CHOH)_3-\underset{\underset{O}{\|}}{C}-NH-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$	128			
VIII	 $CH_2OH(CHOH)_3-\underset{\underset{O}{\|}}{C}-NH-CH-(CH_2)_{11}$	137			

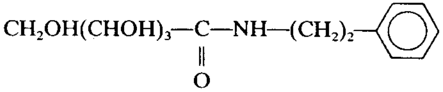
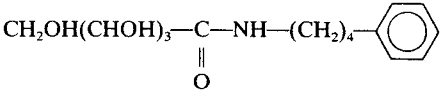
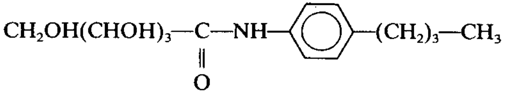
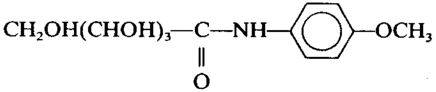
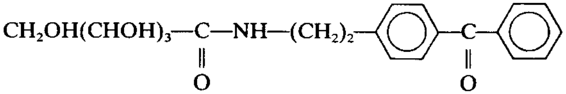
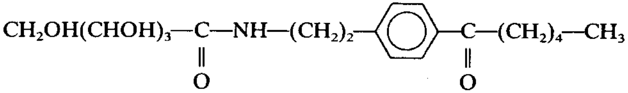
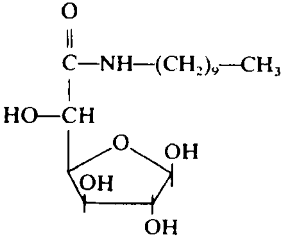
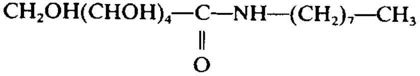
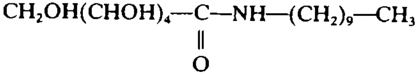
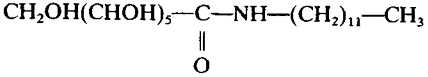
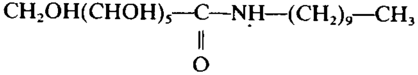
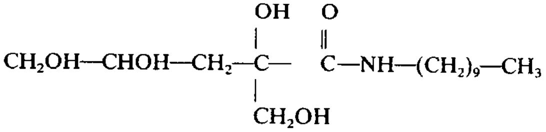
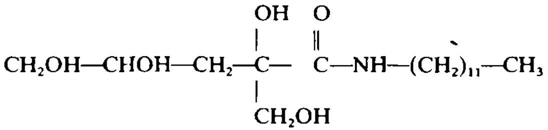
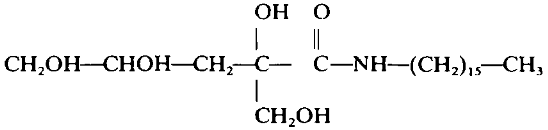
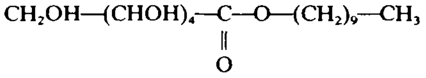
IX		123 (126)			
X		117 (119)			
XI			146 (148)	166 (169)	1665
XII		(149.3^b – 157 – 172)			1668
XIII		(135 ^{b} – 136 ^{b} – 138.3)			
XIV		129.8 (131)			

TABLE II

(*continued*)

Aldonamide		Crystalline compounds $T_{C \to I}$ °C	Liquid crystalline compounds $T_{C \to L}$ °C	$T_{L \to I}$ °C	ν C=O cm^{-1} [c]
XV		124			
XVI	 $CH_2OH(CHOH)_4-\underset{\underset{O}{\|}}{C}-NH-(CH_2)_7-CH_3$		157	158 (161)	1655 (1665)
XVII	 $CH_2OH(CHOH)_4-\underset{\underset{O}{\|}}{C}-NH-(CH_2)_9-CH_3$		157 (160)	180	1620 (1650)
XVIII	 $CH_2OH(CHOH)_5-\underset{\underset{O}{\|}}{C}-NH-(CH_2)_{11}-CH_3$		152 (155)	186 (189)	1620 (1650)
XIX	 $CH_2OH(CHOH)_5-\underset{\underset{O}{\|}}{C}-NH-(CH_2)_9-CH_3$		157 (159)	188 (190)	1655
XX	 $CH_2OH-CHOH-CH_2-\overset{OH}{\underset{CH_2OH}{C}}-\overset{\overset{O}{\|}}{C}-NH-(CH_2)_9-CH_3$		80 [b] −89 (83[b] −91)	105 (107)	1620 (1640)

XXI	 $CH_2OH{-}CHOH{-}CH_2{-}C(OH)(CH_2OH){-}C(=O){-}NH{-}(CH_2)_{11}{-}CH_3$		90 (92)	137 (139)	
XXII	 $CH_2OH{-}CHOH{-}CH_2{-}C(OH)(CH_2OH){-}C(=O){-}NH{-}(CH_2)_{15}{-}CH_3$		98 (100)	155 (157)	1625 (1640)
XXIII	 $CH_2OH{-}(CHOH)_4{-}C(=O){-}O{-}(CH_2)_9{-}CH_3$	97			

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[a] Results obtained with DSC are given in brackets. The other transition temperatures were obtained by microscopic examination.

[b] Crystal-crystal transitions.

[c] Shoulders are given in brackets.

TABLE III

Assignments of the ^{13}C resonances of some aldonamides in DMSO[a] chemical shifts in ppm (δ_{TMS})

Compounds	II	III	IV	V		VI		XVI	XIX	
C=O	172.3	172.3	172.3	172.4		172.3		172.2	173.1	
CHOH	73.8	73.8	73.8	73.8		73.8		73.6	74.6	
	72.6	72.6	72.7	72.7		72.7		72.4	73.5	
	72.0	71.9	72.0	72.1		72.1		71.5	71.9	
								70.1	71.6	
									68.2	
CH_2OH	63.1	63.1	63.2	63.2		63.2		63.4	63.4	
CH_2	38.2	38.3	38.2	38.2		38.2		38.2	38.4	
	28.7	31.1	31.2	31.3		31.3		31.2	31.3	
	28.5	29.0	29.0	29.0	(3C)	29.0	(3C)	29.1	29.0	(3C)
	21.8	28.3	28.7	28.7	(2C)	28.8		28.7	28.8	
		26.2	28.6	26.3		28.7		28.6	28.7	
		21.9	26.3	22.0		26.4		26.3	26.4	
			22.1			22.1		22.0	22.1	
CH_3	13.8	13.8	13.8	13.9		13.9		13.8	13.9	

Compounds	XI	IX	XIV		XXI	
C=O	170.9	172.4	172.5	C=O	174.2	
CHOH	73.9	73.8	73.9	CH_2OH	66.3	
	73.6	72.7	72.8	COH	76.8	
	71.6	71.8	71.8	CH_2	28[b]	
CH_2OH	63.3	63.2	63.2	CHOH	68.2	
				CH_2OH	67.2	
CH-Ar	137.1	139.4	145.1			
	136.3	128.5	134.8			
	128.2	128.3	128.9			
	119.4	126.0	128.0			
CH_2	34.2	39.8	39.4		38.5	
	33.1	35.2	37.7		31.3	
	21.6		35.0		29.0	(5C)
			30.8		28.8	
			23.6		28.7	
			21.9		26.4	
					22.1	
CH_3	13.7		13.7		13.9	

[a] Multiplicity obtained by DEBT pulse sequence.

[b] mean frequency of a multiplet.

present work are in agreement with the structures given in Table II and are listed in Table III.

Infra-red spectra

The frequencies corresponding to the amide absorption are given in Table II. This band, which is usually situated at 1640–1650 cm^{-1} for

TABLE IV

Hydrogen bonds and oxygen-oxygen distances (Å).[7]

Hydrogen bonds		O...O distances	
C=O(1)...H—N	2.13	N ....O(1)	2.977
O(2)—H...O(4)	1.94	O(3)...O(2)	2.738
O(3)—H...O(2)	2.35	O(4)...O(2)	2.736
O(4)—H...O(5)	1.90	O(5)...O(3)	2.804
O(5)—H...O(3)	1.96	O(5)...O(4)	2.742

aliphatic amides represents —CO— groups which are intermolecularly hydrogen bonded to —NH— groups. For some of the compounds investigated, this band occurs in the normal range of frequencies[4] with a small shoulder at a lower frequency (1620 cm^{-1}). In other cases, the main absorption lies at 1620 cm^{-1} with a shoulder at the normal frequency. This lowering of frequency can be assigned to strong hydrogen bonding of the amide carbonyl, probably to —OH rather to —NH groups. On heating the KBr pellet containing the N-decylisosaccharinamide in the sample holder of the IR spectrometer, the amide bond (1620 cm^{-1}) shifts to higher frequencies reaching 1650 cm^{-1} at 145°C. This suggests that intermolecular —CO. . .HN— bonding is predominant at higher temperature.[5] The existence of these different types of hydrogen bonding can be proved by determining the position of the different atoms of the amide molecule in the crystal by X-ray diffraction. As discussed in the next section, this has been done for N-decylribonamide. In this case, the amide I vibration is at the normal position (1640 cm^{-1}); hydrogen bonding has been identified between —CO— and —NH— groups of neighbouring molecules. Further work is in progress along this line.

Concerning N-phenylamides (XI and XII) the observed shift to higher frequency as compared with N-alkylamides is in agreement with the data of the literature.[4]

Thermal behaviour of the neat amides

The different amides listed in Table I have been examined by hot stage polarizing microscopy (using a constant heating rate). The observed transition temperatures are listed in Table II. A liquid crystal phase was shown to form in the linear N-alkylribonamides (III to VI), gluconamides (XVI to XVIII), heptonamide (XIX) and in the N-p-butylphenylribonamide (XI) which contains a phenyl group adjacent to the nitrogen atom. A normal crystalline solid-isotropic liquid melting point was observed for the other products. The observed textures of the liquid crystal phases are the same as those reported previously for N-decylribonamide. Homeotropic areas corresponding to uniaxial planar regions appear after the first transition either spontaneously or can be induced by small movement of the cover glass. They contain spherulites with positive optical sign but spherulites with negative sign are also observed. The planar areas transform into mosaíc regions under vigorous movement of the cover glass. Also "bâtonnets" precipitate on rapid cooling from the isotropic phase. Some typical textures are shown in Figure 1. As reported previously in the case of N-decylribonamide, all the textures reported by Rosevear[6] for the lamellar phase have been observed but none of the textures reported for the rodlike hexagonal middle phase could be detected. We thus identify the mesophases formed by the amides of Table II as lamellar. The recent determination of the crystal structure of N-decylribonamide has clearly demonstrated[7] the existence of monolayers of strongly hydrogen bonded molecules (Figures 2 and 3). It is most probable that the arrangement of molecules which is prevalent in the crystal will be essentially maintained on passing from the crystal to the highly viscous lamellar phase. Differential scanning calorimetry (Table II) reveals the presence of the same transitions usually 2°C higher than when measured with the microscope. This is due to the higher heating rate used by DSC. For some products, (XII, XIII and XX), multiple first order transitions corresponding to crystal-crystal transitions were observed by DSC. The temperature range of stability of the lamellar phase as observed with the microscope is very narrow (1°C) for compounds III and XVI. The two first order transitions $T_{C \to L}$ and $T_{L \to I}$ could not be resolved by DSC during an heating cycle for these compounds but they could be very easily observed by DSC and by microscopy on cooling owing to the pronounced supercooling of the $(L \to C)$ transition.

RELATION BETWEEN CHEMICAL STRUCTURE AND THERMAL MESOMORPHISM

As reported above and in Table II, an ester and twenty two amides have been examined by DSC and with the polarizing microscope. A lamellar mesophase is formed during heating for several of them. The results shown in Table II give indications of the structural requirements for thermal mesomorphism in this family of compounds. N-decylribonamide has been previously shown to have an organized

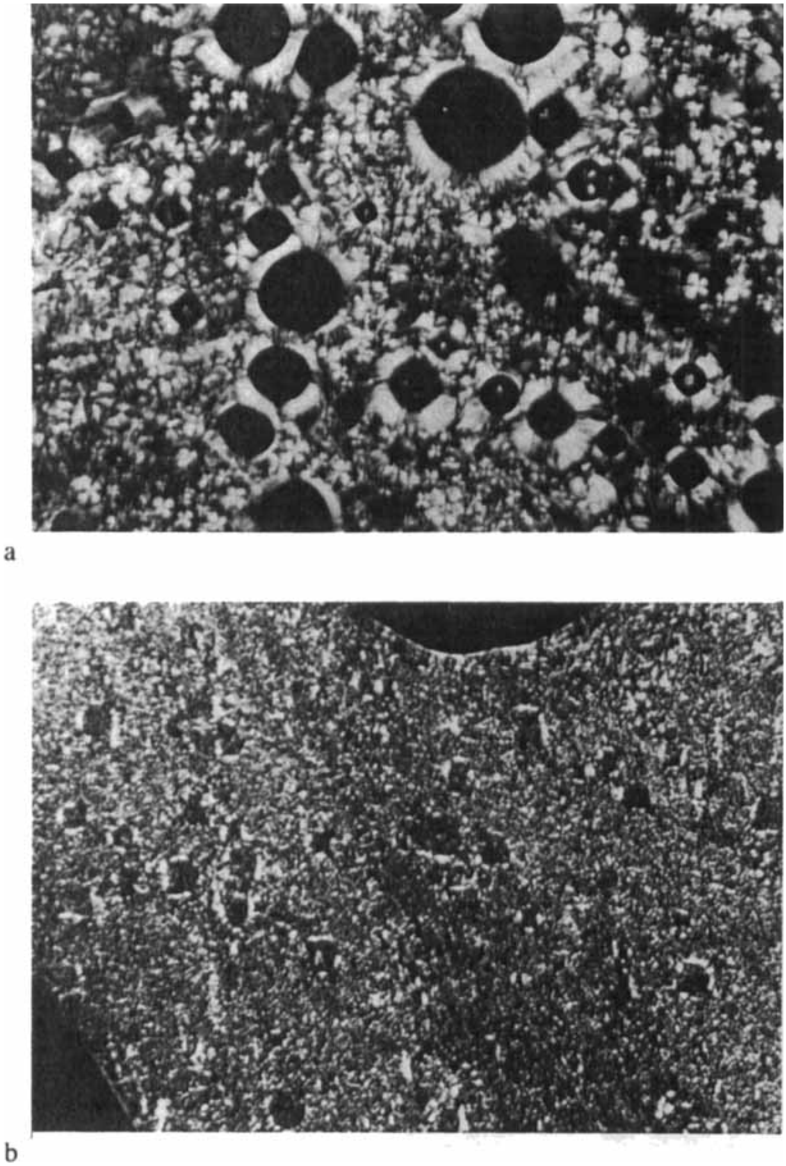


FIGURE 1 N-Dodecylisosaccharinamide.
a) Observed at 125°C between crossed polars: planar texture—spherulites with positive optical sign
b) Mosaic texture observed at 110°C after vigorous movement of the cover glass

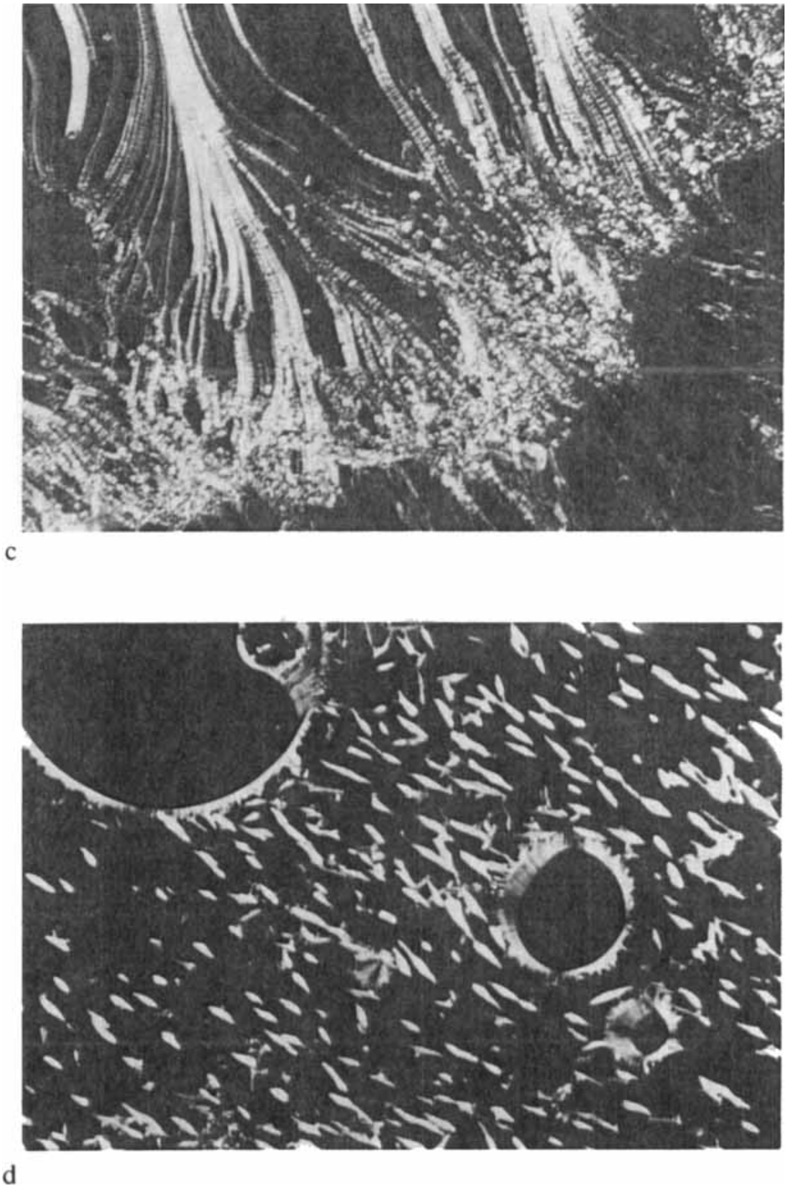


FIGURE 1 (continued)
c) Oily streaks observed at 131°C
d) Formation of "bâtonnets" on rapid cooling from the isotropic phase.

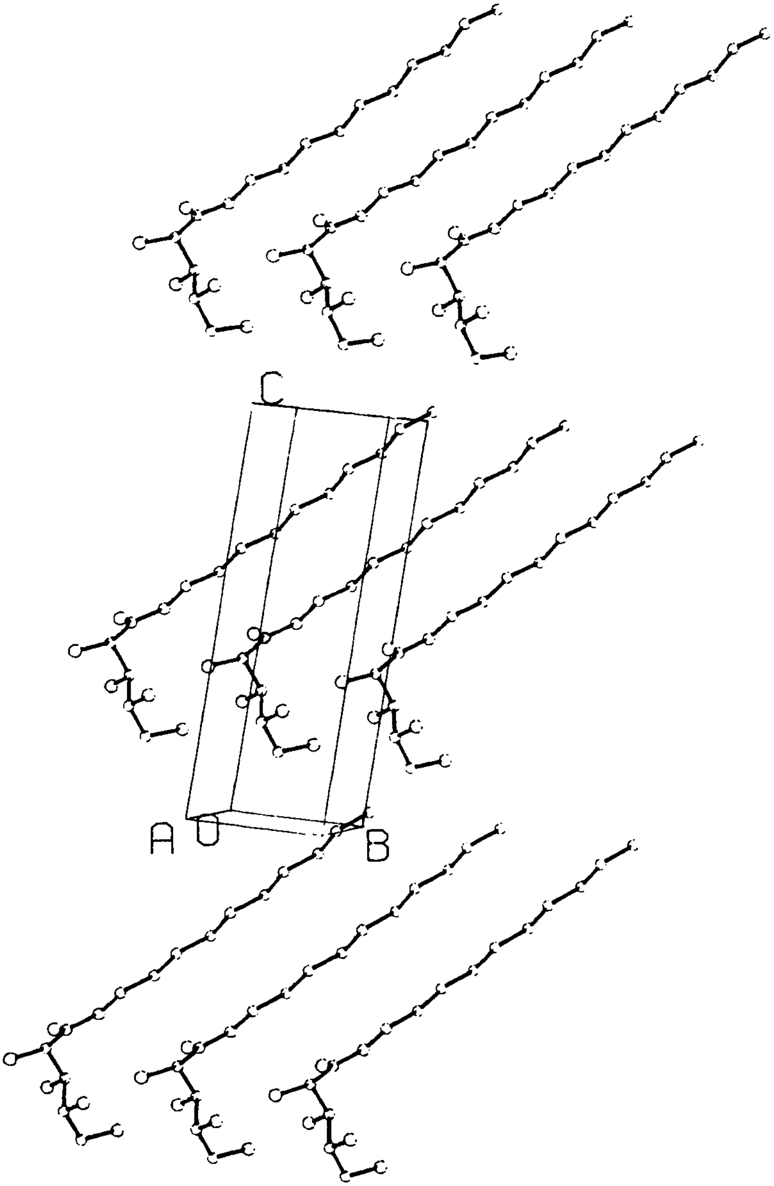


FIGURE 2 Packing of the N-decylribonamide in the unit cell: monolayer arrangement.[7]

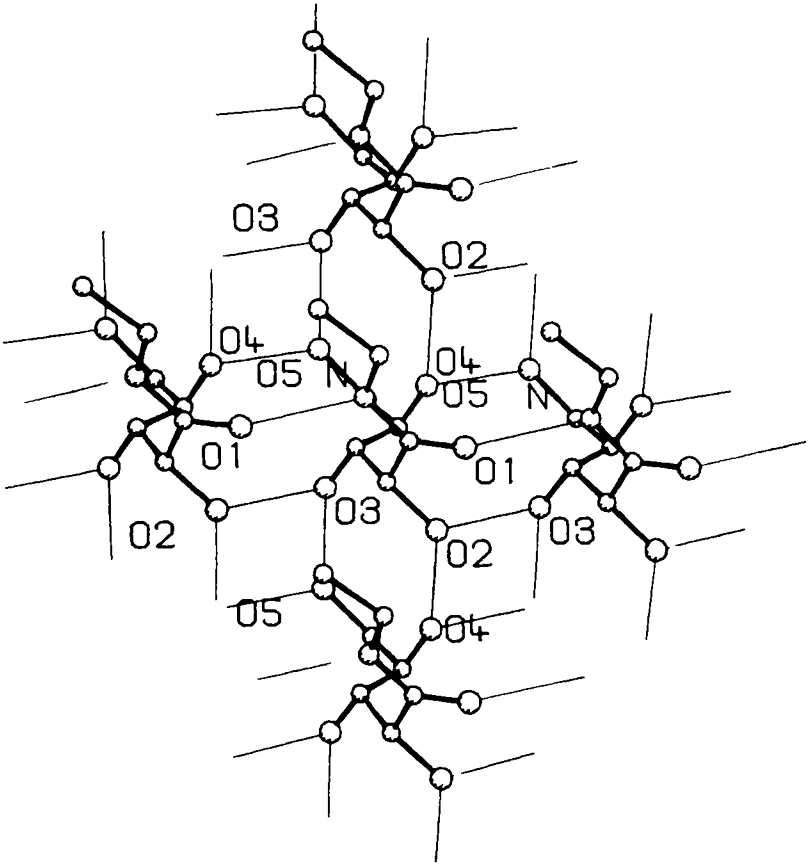


FIGURE 3 View of the N-decylribonamide monolayer with its strongly hydrogen bonded molecules.[7]

lamellar liquid structure between 99° and 151°C. When the amide group is replaced by an ester group (XXIII), no mesomorphism can be detected. If now the length of the linear hydrocarbon chain is increased to C-12 (VI) or decreased to C-8 (IV), a mesophase is observed over a rather broad temperature range. For N-heptylribonamide (III) mesophase formation is still observed between 94° and 95°C but N-pentyl- and N-butylribonamide (II and I) do not give liquid crystal phases. If the ribonic residue is replaced by a gluconic residue (XVI to XVIII) the $T_{C \to L}$ and the $T_{L \to I}$ transitions occur at higher temperatures for a given alkyl chain length but the temperature range is narrower. If the gluconic residue is replaced by an heptonic residue (XIX), $T_{C \to L}$ and $T_{L \to I}$ do not rise appreciably. If now the linear gluconic residue is replaced by the C-6 isosaccharinic structure (XX to XII) which is branched and in which one —OH group is replaced by —H, the values of $T_{C\to L}$ and $T_{L\to I}$ are lower than for the ribonic series. The thermal degradation of the isosaccharinic derivatives, as observed by the yellowing of the products, is much less than that of the other products since the elimination of water molecules between neighbouring —OH groups is much less probable in these compounds. Indeed, the secondary and tertiary —OH groups respectively situated on C-2 and C-4 are separated by a —CH$_2$— group whereas the other aldonic residues possess at least three neighbouring secondary —OH groups. Comparison of the transition temperatures as a function of the length of the alkyl chain and of the nature of the aldonic residue is easy by examination of Figure 4 which

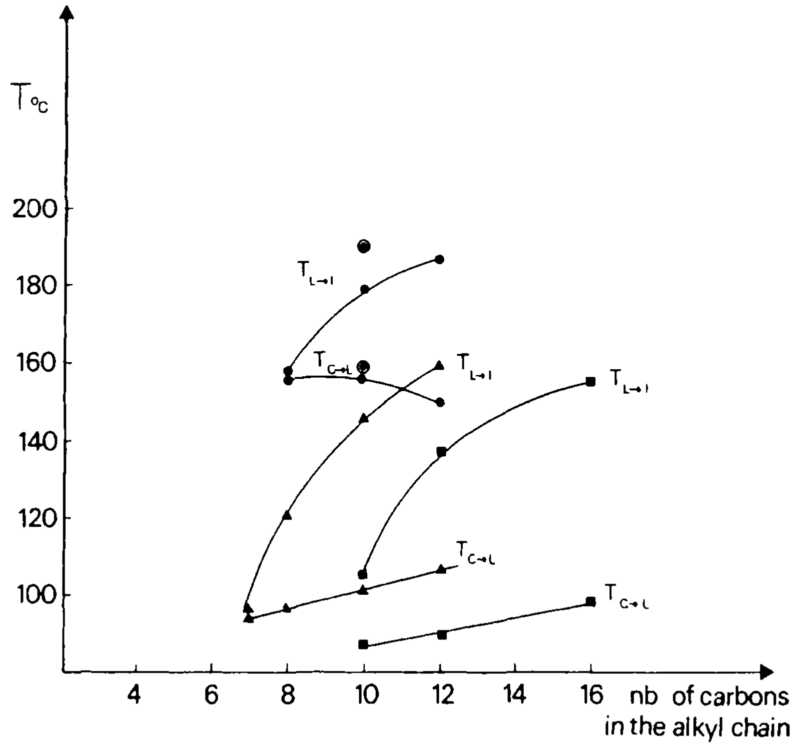
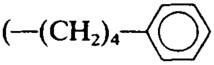
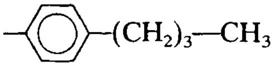


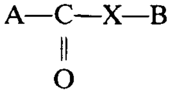
FIGURE 4 Transition temperatures of the different aldonamides as a function of the length of the alkyl chain.

▲ ribonamides
● gluconamides
◉ heptonamides
■ isosaccharinamides

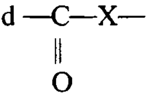
shows the experimental results graphically. If the hydrophilic group is cyclic instead of linear (XV) no liquid crystal phase forms on heating.

Modification of the structure of the hydrocarbon chain of the aldonamide has been studied. If the alkyl chain is not linear, no mesomorphism is observed (VII and VIII). Phenyl groups have been introduced in compounds IX to XIV. No mesophase could be detected above the melting point of these compounds with the exception of compound XI for which the aromatic group is situated next to the amide group. If the position of the aromatic group is changed ( in X instead of  in XI), the lamellar phase does not form.

We conclude that three conditions have to be fulfilled for thermal mesomorphism in compounds of general formula



$$A-\underset{\underset{\displaystyle O}{\|}}{C}-X-B$$

where A is a polyol hydrophilic residue, B an alkyl or arylalkyl hydrophobic chain and  $-\underset{\underset{\displaystyle O}{\|}}{C}-X-$ a functional group. Firstly, the functional group must be an amide and not an ester. Secondly, B must be a linear chain with a minimal length (C-8 for the gluconic series and C-7 for the ribonic series). If there is an aromatic group in B, it must be situated next to X. Thirdly, A must not be a cyclic carbohydrate.

In a preceding paper, a bilayer structure was proposed for the lamellar mesophase. It was suggested that the amide was in the *trans*-configuration and the bilayer was stabilized by hydrophobic interactions between the hydrocarbon chains and by H-bonding between neighbouring amide groups and between neighbouring aldonic residues. Recent single crystal X-ray structure determination of N-decylribonamide[7] has however shown that the molecules in the crystal are actually arranged in monolayers instead of bilayers (Figure 2). The monolayer is stabilized by hydrophobic interactions between the alkyl chains and by hydrogen bonds between the hydrophilic parts of neighbouring molecules. The unit cell is triclinic (space group P1). The parameters of the unit cell are: $a = 4.825$, $b = 5.452$, $c = 16.100$ Å,

$\alpha = 87.03$, $\beta = 93.10$, $\gamma = 96.10°$. The *trans*-configuration of the amide and the strong hydrogen bonding is clearly apparent in Figure 3. Each hydroxyl oxygen atom is involved in two hydrogen bonds. There are thus eight hydrogen bonds of this type per molecule. The carbonyl oxygen and the nitrogen atom are also each involved in one hydrogen bond. The crystal is thus stabilized by ten hydrogen bonds per molecule. The length of these hydrogen bonds is given in Table IV. The presence of monolayers instead of bilayers in the crystal certainly lowers the energy necessary to separate the layers at the transition from crystal to lamellar phase: the interaction between the hydrocarbon chains of one layer and the polar aldonic residue of the next one is indeed weak. We feel that the general organization of the lamellar phase is most certainly similar to that of the crystal. Indeed, large displacements of the molecules are improbable on passing from the crystal to the viscous lamellar phase. Molecular organization of the smectic A type can be anticipated from the identification of the observed textures. Direct determination of the structure of the mesomorphic phase will be performed soon. Single crystal structure determinations of other amides are now in progress. The most interesting problems to elucidate are the effect of shortening, branching, and phenyl substitution in the alkyl chain and of changing the functional group from amide to ester, on the relative position of the molecules in the unit cell.

CONCLUSION

Strict conditions have to be obeyed for the formation of lamellar mesophases in N-substituted aldonamides. Linearity and minimum length is required for the amine residue. Any aromatic ring has to be situated next to the amide group. The aldonic residue can be either linear or branched but not cyclic. Single crystal studies imply a monolayer arrangement of the molecules in the mesophase. The lamellae are stabilized by hydrogen-bonding and hydrophobic interactions between the molecules in the *trans*-configuration.

Acknowledgments

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