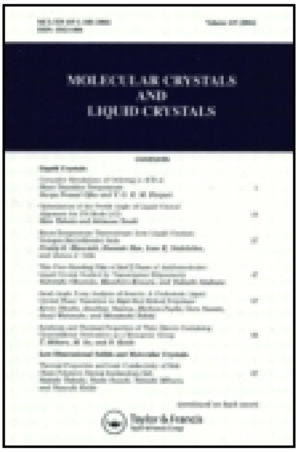

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N-Substituted Aldonamides V X-Ray Diffraction Study of the Crystal and Thermotropic and Lyotropic Mesophases of N-Alkylribonamides

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N-Substituted Aldonamides V X-Ray Diffraction Study of the Crystal and Thermotropic and Lyotropic Mesophases of N-Alkylribonamides

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The structure of two N-alkylribonamides both in the anhydrous state and in concentrated water solution has been studied by X-ray diffraction. A Lamellar Crystalline, a Lamellar Liquid-Crystalline and a Cylindrical Hexagonal Liquid-Crystalline Structures have been found. The influence of temperature and of water concentration on the geometrical parameters of the mesophases has been established. The organization of the molecules in the three structures is described and a step by step melting behavior is proposed for the N-alkylaldonamides.

INTRODUCTION

A broad series of N-substituted aldonamides differing in the length, branching and cyclization of both aldonic and the hydrocarbon parts of the molecules have been synthetized.[1,2] A Lamellar Thermotropic phase and Lamellar and/or Hexagonal Lyotropic phases have been identified by examination of the textures formed as a function of temperature using the polarizing microscope.[1-4]

The relationship between the mesogenic properties and the molecular structure of these compounds has been established. Mesophase formation requires at least 7 carbon atoms in the alkyl chain. Branching of the alkyl chain inhibits the formation of thermotropic and lyotropic phases. Cyclization is not a restriction for the formation of lyotropic phases as it is for the formation of thermotropic phases in the neat compound. The temperature and concentration range of existence of the lyotropic lamellar and hexagonal phases is a function of the hydrophilic-hydrophobic balance of each molecule: a lengthening of the alkyl chain increases the hydrophobic character and hence favours the formation of lamellar mesophases;

on the contrary, an increase in the length or branching of the aldonic group increases the hydrophilicity and hence the stability of the hexagonal phase.[3,4]

In order to obtain informations about the molecular organization in the lyotropic and thermotropic mesophases of N-substituted aldonamides and about the structural characteristics of these mesophases we have undertaken a X-ray diffraction investigation of two N-alkylribonamides: the N-octylribonamide (5N8) and the N-decylribonamide (5N10). Both compounds exhibit a lamellar thermotropic mesophase, but, if 5N8 exhibits both a lamellar and a hexagonal lyotropic mesophase, 5N10 exhibits only a hexagonal lyotropic mesophase. In the present paper we report the results of our X-ray diffraction study to describe the structure of the four phases observed (Lamellar Crystalline, Lamellar Thermotropic, Lamellar Lyotropic and Hexagonal Lyotropic) and suggest a mechanism of formation of the mesophases.

EXPERIMENTAL

Synthesis

N-octylribonamide $CH_3—(CH_2)_7—NH—CO—(CHOH)_3—CH_2OH$ and N-decylribonamide $CH_3—(CH_2)_9—NH—CO—(CHOH)_3—CH_2OH$ were synthesized at room temperature by addition of stoichiometric amounts of *n*-octylamine and *n*-decylamine to a methanol solution of D (+)-ribonic acid-γ-lactone.

Mesomorphic Gels

Known amounts of N-alkylaldonamides and water were homogenized in sealed tubes at temperatures slightly higher than the melting temperature, then cooled to room temperature and transferred into tight cells for X-ray studies. After X-ray experiments, the concentration of each sample was checked by evaporation to dryness under vacuum.

X-ray Diffraction

X-ray Diffraction was performed under vacuum with a Guinier-type focussing camera equipped with a bent quartz monochromator giving a linear collimation and a device for recording diffraction patterns at various temperatures between 25 and 200°C with an accuracy of ±1°C.

RESULTS

The two N-alkylribonamides have been studied at different temperatures in the anhydrous state and in water solutions with concentrations corresponding to the domain of existence of the lamellar and hexagonal mesophases determined by polarization microscopy.[4] The corresponding phase diagrams are given in Figures 1a and 1b.

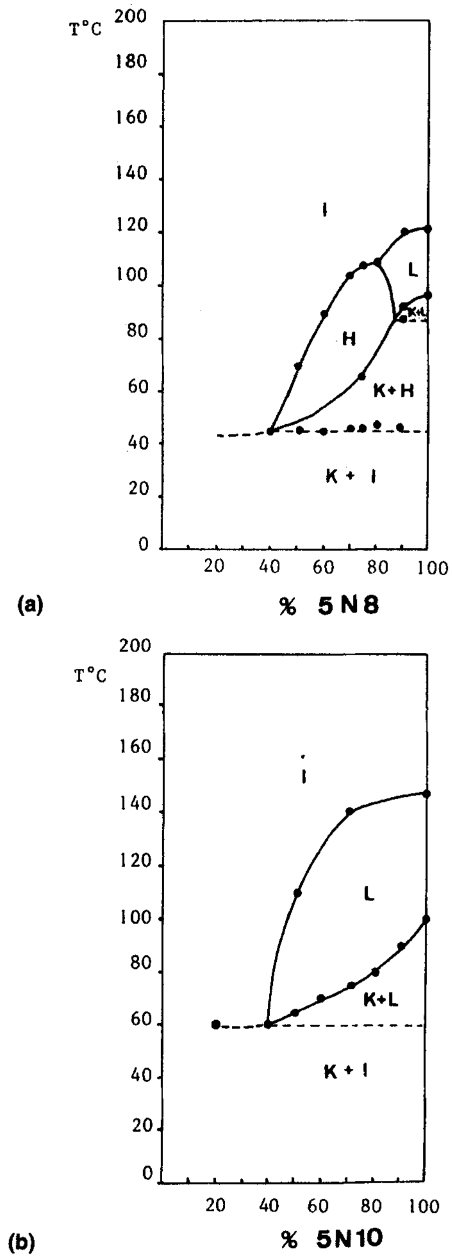

FIGURE 1 Phase diagram of 5N8 (1a) and 5N10 (1b).

1. Description of the Structure

As in the case of soaps[5–7] and many other amphiphiles[8–10] two regions can be distinguished on the X-ray patterns:

The central region (low angles) that presents a set of sharp reflections whose

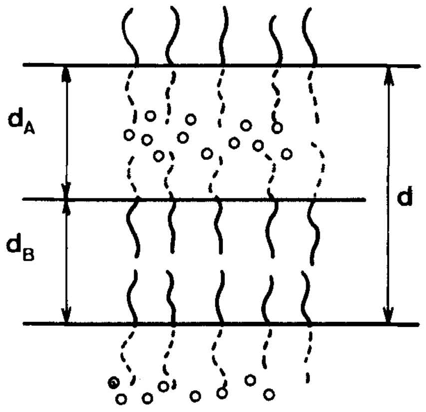

FIGURE 2 Schematic representation of the lamellar structure.

∼ paraffinic chain

- - - saccharidic chain chain, O O O water.

Bragg distance ratios allow the determination of the structural type: Lamellar, Hexagonal or Cubic.

The external region (wide angles) that exhibits a set of sharp lines if the paraffinic chains are crystallized and a diffuse band if the paraffinic chains are disorganized and "liquid-like."

All X-ray patterns obtained in this work can be classified in 3 families corresponding to 3 types of structures.

The first family exhibit in the low angle region a set of sharp lines with Bragg spacings in the ratio 1:2:3 . . . characteristic of a lamellar structure and in the wide angle region a set of reflections characteristic of crystallized paraffinic chains.

The second family exhibit in the low angle region a set of sharp lines with Bragg spacings in the ratio 1:2:3 . . . characteristic of a lamellar structure and in the wide angle region the diffuse band characteristic of liquid paraffinic chains.[5]

The third family exhibit in the low angle region a set of sharp lines with Bragg spacings in the ratio $1{:}\sqrt{3}{:}\sqrt{4}$ . . . characteristic of a cylindrical hexagonal structure and in the wide angle region the diffuse band characteristic of liquid paraffinic chains.[5]

The N-alkyl ribonamide molecules consist of two parts: a hydrophilic part A = $NH—CO—(CHOH)_3—CH_2OH$ and a hydrophobic part B = $CH_3—(CH_2)_n$. The two parts of the molecule are incompatible and tend to segregate at the molecular level, so we can describe the two lamellar structures and the hexagonal structure as follows.

The lamellar crystalline structure consists of plane, parallel, equidistant sheets; each sheet, of thickness **d**, results from the superposition of two layers; one, of thickness $\mathbf{d}_A$, contains the hydrophilic saccharidic chains, while the other, of thickness $\mathbf{d}_B$, contains the hydrophobic and crystallized paraffinic chains.

The lamellar liquid-crystalline structure (thermotropic or lyotropic) consists of plane, parallel, equidistant sheets: each sheet, of thickness **d**, results from the superposition of two layers; one, of thickness $\mathbf{d_A}$, contains the hydrophilic saccharidic chains and the water, while the other, of thickness $\mathbf{d_B}$, contains the liquid hydrophobic paraffinic chains (Figure 2).

The hexagonal structure consists of long and parallel cylinders of radius **R**, assembled in a hexagonal array of parameter **D**. The cylinders are filled with the quasi liquid paraffinic chains, while the space between the cylinders is occupied by the hydrophilic saccharidic chains and the water (Figure 3).

The lattice parameters: d for the lamellar structures and D for the hexagonal structure were obtained directly from the X-ray patterns. The other parameters: d_A, d_B, R, S_L and S_H (the average surface occupied by a chain at the interface for the lamellar and hexagonal structures respectively) were obtained using the following formulae based on simple geometrical considerations:

$$d_B = d\left(1 + \frac{CX_AV_A + (1 - C)V_S}{C(1 - X_A)V_B}\right)^{-1} \tag{1}$$

$$d_A = d - d_B \tag{2}$$

$$S_L = 2M_BV_B/Nd_B \tag{3}$$

$$R^2 = \frac{D^2\sqrt{3}}{2\Pi}\left(1 + \frac{CX_AV_A + (1 - C)V_S}{C(1 - X_A)V_B}\right)^{-1} \tag{4}$$

$$S_H = 2M_BV_B/NR \tag{5}$$

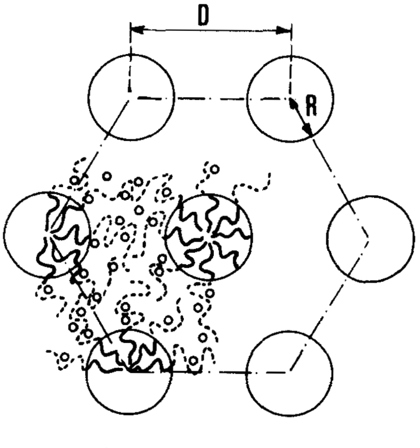

FIGURE 3 Schematic representation of the hexagonal structure.

paraffinic chain

saccharidic chain, ○○○ water.

where: C is the weight content of N-alkylaldonamide in solution; X_A is the weight fraction of hydrophilic saccharidic chains A; V_A is the specific volume of the hydrophilic saccharidic chains A[9,11]; V_B is the specific volume of the hydrophobic paraffinic chains B[9,11,12]; V_S is the specific volume of water; M_B is the molecular weight of the paraffinic chains and N is the Avogadro number.

2. Influence of the Water Concentration

When water is added to the thermotropic lamellar mesophase of anhydrous N-alkylribonamides, the lamellar structure swells. When the amount of water exceeds a limit value depending upon the molecular characteristics of the ribonamides the lamellar mesophase disappears or transforms into a cylindrical hexagonal mesophase according to the length of the alkyl chains.

In order to illustrate this behavior we have plotted on the Figures 4 and 5 the variations of the geometrical parameters of the lamellar and hexagonal structures of the N-decylribonamide (5N10) and N-octylribonamide (5N8), as a function of the water concentration $(1 - C)$.

It can be seen that when the water concentration increases: for the lamellar structure the total thickness **d** of a sheet, the thickness $\mathbf{d_A}$ of the hydrophilic layer and the average surface **S** per molecule at the interface all increase while the thickness $\mathbf{d_B}$ of the hydrophobic paraffinic layer decreases. For the hexagonal structure the distance **D** between two neighboring cylinders and the average surface **S** per molecule at the interface both increase while the radius **R** of the hydrophobic paraffinic cylinders decreases.

Such a behavior can be easily explained; when water is added to the mesophase the hydrophilic domains swell, the surface per molecule at the interface increases

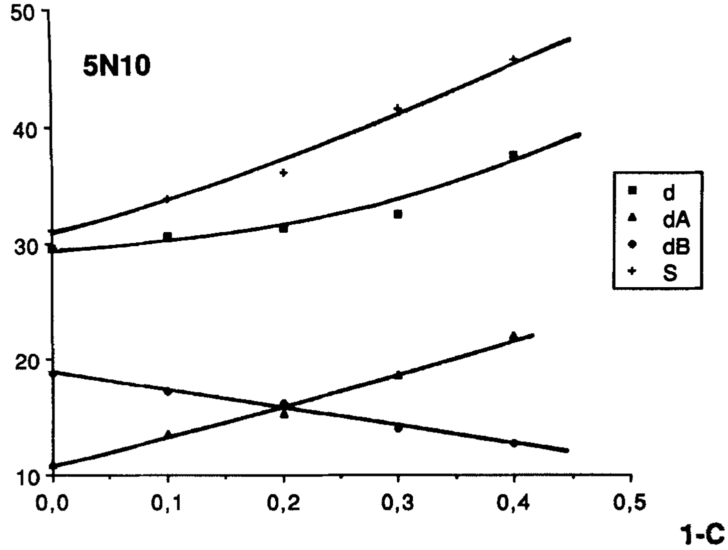

FIGURE 4 Variation with water concentration of the structural parameters of the lamellar mesomorphic structure exhibited by 5N10 at 110°C: □ = d; Δ = d_A; ○ = d_B; * = S_L; d, d_A, d_B in A; S_L in A^2.

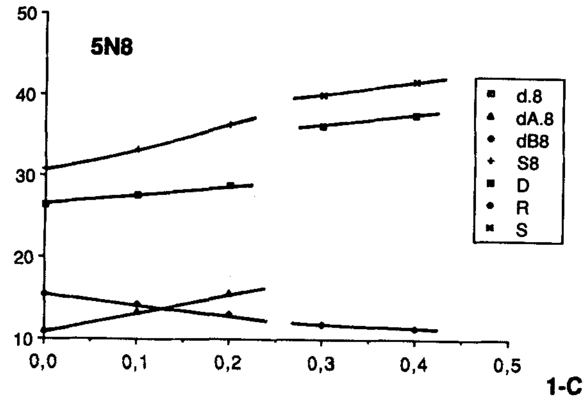

FIGURE 5 Variation with water concentration of the structural parameters of the lamellar and hexagonal mesomorphic structures exhibited by 5N8 at 110°C and 85°C respectively: □ = d; Δ = d_A; ○ = d_B; + = S_L; ■ = D; ● = R; × = S_H; d, d_A,d_B, D, R in A; S_L, S_H in A.

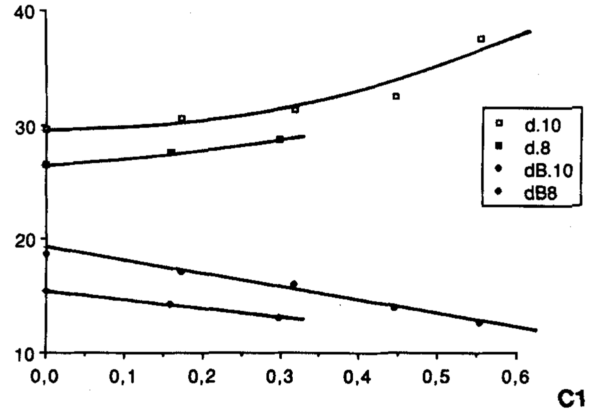

FIGURE 6 Variation, with the water content C1 of d and d_B for 5N10 (empty symbols) and 5N8 (black symbols); d and d_B in A.

and as the paraffinic chains have to keep a constant density the parameter of the hydrophobic domains (d_B or R) decreases.

3. Influence of the Length of the Paraffinic Chains

In order to show the influence of the length of the paraffinic chains, we have plotted on the Figures 6 and 7 the variation of the geometrical parameters of the lamellar mesophases of the N-octyl- and N-decylribonamides as a function of the water content C_1 of the hydrophilic domains

$$C_1 = (1 - C)/(1 - C + CX_A) \tag{6}$$

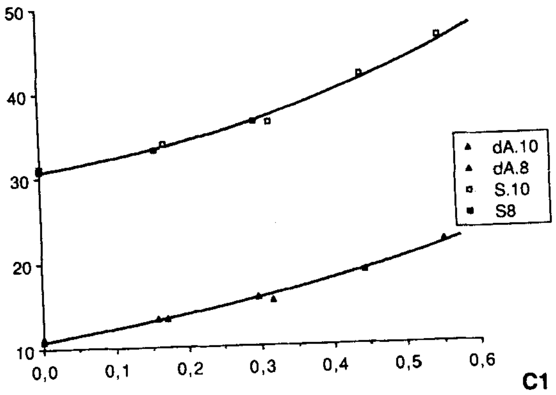

FIGURE 7 Variation, with the water content C1 of the hydrophilic domains, of d_A and S for 5N10 (empty symbols) and 5N8 (black symbols); d_A in A; S_L in A^2.

It can be seen that the total thickness **d** of a sheet and the thickness $\mathbf{d_B}$ of the hydrophobic paraffinic layer both increase with the length of the alkyl chains while the parameters of the hydrophilic domains namely the thickness $\mathbf{d_A}$ of the hydrophilic saccharinic layer and the surface **S** per molecule at the interface are independent of the length of the paraffinic chains.

4. Influence of the Temperature

The N-decyl ribonamide (5N10) was studied in the lamellar thermotropic phase between 105°C and 135°C.[3,4] The thickness d of the lamellae decreases when the temperature increases and the thermal contraction coefficient K is 4.53×10^{-4}

$$K = \Delta d/d\cdot\Delta T \tag{7}$$

DISCUSSION

We have shown that N-alkylribonamides exhibit lamellar crystalline and lamellar and hexagonal liquid-crystalline structures. We shall now discuss the organization of the molecules in these structures.

1. Lamellar Crystalline Structure

We have found that anhydrous N-decylribonamide exhibit at room temperature a Lamellar Crystalline Structure with the following parameters; d = 33 Å, d_A = 13 Å, d_B = 20 A, S = 26 Å^2.

The length **l** of the paraffinic chains in a fully extended all trans conformation measured on CPK models is 12.7 Å, so d_B = 1.57 **l**.

There are two possibilities for explaining this value: a partial interdigitation of paraffinic chains perpendicular to the lamellae, or a double layer of tilted paraffinic chains with an angle of tilt α = 38° (α is given by $\cos \alpha = d_B/2\mathbf{l}$). With a partial interdigitation of the alkyl chains it is difficult to fill the hydrophobic layer in a homogeneous way. On the contrary tilted and parallel paraffinic chains give a perfect packing of the molecules and the surface occupied by a paraffinic chain in a plane perpendicular to its axis is 21 Å^2 in good agreement with the average section of a crystalline paraffinic chain.

The thickness d_A = 13 Å of the hydrophilic saccharinic layer is also in good agreement with a double layer of ribonamide units as measured on CPK models.

Therefore, in a sheet of thickness d of the lamellar crystalline structure of N-alkylribonamides, the hydrophilic layer of thickness d_A consists of a bilayer of the ribonic moiety of the molecules and the hydrophobic layer of thickness d_B consists of a bilayer of tilted all trans paraffinic chains. The overall molecular conformation is V-shaped with both the alkyl chain and the ribonyl moieties fully extended the bend occurring at the amide link and the molecules being packed head-to-head.

Monolayer head-to-tail structures were found for monocrystals of N-decylribonamide obtained by evaporation of tetrahydrofuran solution,[13] monocrystals of N-heptyl, N-octyl and N-decylgluconamides obtained from methanol solution,[14,15] while head-to-tail monolayer or head-to-head bilayer structures were obtained for crystals of N-undecylgluconamide depending upon crystallization conditions.[16] So it seems that the monolayer or bilayer character of the lamellar crystalline structure of N-alkylaldonamides would be governed by the crystallization conditions and the thermal history of the sample.

2. Lamellar Liquid-Crystalline Structure

At the transition between the lamellar crystalline and the lamellar liquid-crystalline phases, the reflections characteristic of crystalline paraffinic chains observed at wide angles on X-ray patterns disappear. The surface occupied by a molecule at the interface between hydrophilic and hydrophobic layers suddenly increases (from 26 A^2 to more than 31 Å^2 for N-decylribonamide) and becomes similar to that observed for the Neat Phase of alkali metal soaps.[17–20] Furthermore the thermal contraction coefficient of N-decylribonamide $K = 4.5 \cdot 10^{-4}$ is similar to that of the Potassium Decanoate: $K = 6.2 \cdot 10^{-4}$.[20]

For all these reasons we can conclude that in the lamellar mesophase of N-alkylribonamides the paraffinic chains are in a "liquid-like" state. So the comparison of the length of the molecule in an extended all-trans conformation with the thickness of the lamellae is not realistic and if the classification in mono and bilayer smectic has still some signification in the case of liquid-like paraffinic chains, the lamellar mesomorphic structure of N-alkylribonamides is of the bilayer type.

A bilayer head-to-head structure was also found for the lamellar thermotropic phase of N-undecylgluconamide.[16] Furthermore both interdigitated and bilayer smectic structures were proposed for some straight chain carbohydrate amphiphiles.[21,22]

When water is added to the anhydrous thermotropic mesophase of N-octyl- and N-decylribonamides (Figures 4 and 5) there is no discontinuity in the variation of the geometrical parameters of the lamellar structure but only a swelling of the layer containing the hydrophilic ribonamide moieties, so the thermotropic and lyotropic lamellar structures are of the same type.

3. Hexagonal Liquid-Crystalline Structure

As in the case of amorphous block copolymers[23] and amphiphilic lipopeptides,[24] the type of mesomorphic structure adopted by N-alkylribonamides is determined by the ratio of the volumes of the hydrophilic and hydrophobic domains. So when water is added to the lamellar mesophase one observes, depending upon the length of the paraffinic chains, only a lamellar structure or a lamellar structure and a cylindrical hexagonal one.

The hexagonal structure of N-alkylribonamides is similar to that of alkali metal soaps. For instance both N-octylribonamide and potassium octanoate exhibit at 85°C in concentrated water solution a hexagonal structure in which the radius R of the paraffinic cylinders takes values between 11 and 12 Å.[7,19]

4. Thermic Behavior

We have already seen that at the transition between the lamellar crystalline and the lamellar liquid-crystalline phase the paraffinic chains of the N-alkylribonamides melt and the value of the surface occupied by a molecule at the interface increases from a value typical of a crystalline paraffinic chain to a value typical of a liquid paraffinic chain. Furthermore, the average surface $\mathbf{S}$ for a molecule at the interface and the thickness $\mathbf{d}_A$ of the saccharidic layer are independent of the length of the paraffinic chains (see Figures 6 and 7) but depend upon the nature of the saccharidic moiety (calculations of $\mathbf{d}_A$ and S of N-alkylgluconamides using formulae 1 to 3 and the value of $\mathbf{d}$ given in reference 22 gives $\mathbf{d}_A = 12.5$ Å and $\mathbf{S} = 36$ Å^2 for alkylgluconamides instead of $\mathbf{d}_A = 11$ Å and $\mathbf{S} = 31$ Å^2 for N-alkylribonamides).

Therefore we suggest that the transition between the Lamellar Crystalline Structure and the Lamellar liquid-Crystalline Structure results from the melting of the paraffinic chains of the N-alkylaldonamides and that in the Lamellar Mesophase (thermotropic or lyotropic) the alkyl chains are "liquid-like" while the interactions between the saccharidic parts of the molecules (probably mainly through hydrogen bonds) are responsible for the stability of the mesomorphic structures. When the temperature increases further, the paraffinic chains contract in the direction perpendicular to the interface, the average surface S per molecule increases, the distance between saccharidic units increases reducing the intermolecular interaction forces and at last the thermal agitation forces overcome the cohesion forces and an isotropic phase replaces the mesophase. So N-alkylaldonamides exhibit a step by step melting as anhydrous alkali metal soaps do.[17–20]

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