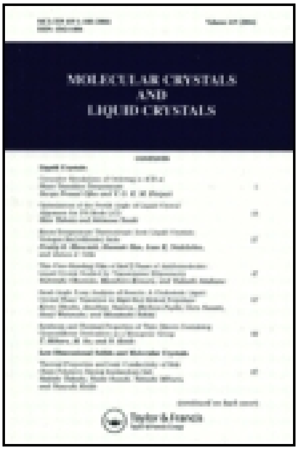

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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To cite this article: Gervais Chapuis , Kurt Schenk & Javier Zuniga (1984): Temperature Induced Phase Transitions in Lipid Bilayer Models, Molecular Crystals and Liquid Crystals, 113:1, 113-121

To link to this article: http://dx.doi.org/10.1080/00268948408071676

Mol. Cryst. Liq. Cryst., 1984, Vol. 113, pp. 113-121
0026-8941/84/1134-0113/$15.00/0

Printed in the United States of America

TEMPERATURE INDUCED PHASE TRANSITIONS IN LIPID BILAYER MODELS

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Abstract Different types of n-alkyl containing compounds have been studied by temperature controlled single crystal x-ray diffraction. They crystallize in layers of alkylammonium ions alternating with layers of counter ions. The organic layers mimic liquid crystals of the smectic type or bilayers as found in biomembranes. These compounds exhibit numerous phase transitions which are due mainly to different chain conformations. In one example, the transitions preceding the melting of the chains has been analysed step by step and shows the evolution of the various chain conformations. In another example, evidence has been found of the separation of the chains from an intercalated type of packing to a non-intercalated type.

INTRODUCTION

Numerous examples of materials can be found in nature which consist of 2-dimensional nets of organic residues such as aliphatic chains : the central part of lipid bilayers, various liquid crystals and polymer types. The amphiphatic character of these materials is responsible for the formation of layers, some of them with "crystalline" periodicity. To study their thermal characteristics by single crystal x-ray diffraction, we have used models of smectic bilayer of the type $(C_nH_{2n+1}NH_3)_2MCl_4$ or $C_nH_{2n+1}NH_3Cl$ with M = Cu, Cd, Zn and n > 6. These substances crystallize in layers of n-alkylammonium alternating with layers of the counter ion. Hydrogen bonds between the Cl-atoms and the ammonium ions are responsible for the packing of the layers in the third dimension. Numerous phase transition can be observed near room temperature in analogy to biomembranes for example.

STRUCTURAL CHARACTERISTICS OF THE ORGANIC LAYERS

Two main groups can be distinguished depending on the nature of the organic layer. The family of the type $(C_nH_{2n+1}NH_3)_2ZnCl_4$ (short CnZn) and $C_nH_{2n+1}NH_3Cl$ (CnCl) belong to the intercalated type as the layer is formed by chains attached alternatively to both neighbouring layers as represented in fig. 1a)

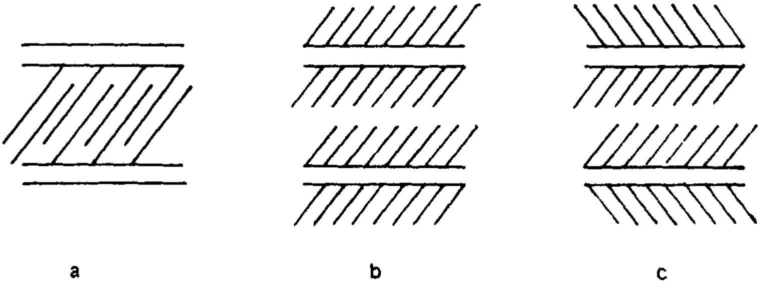

FIGURE 1. Various packing types of organic layers.

The other group represented by CnCd or CnCu belongs to the non-intercalated type (fig. 1b, 1c). It is the magnitude of the translation periods of the layer formed by the counter ion (connected $CdCl_6$ octahedra, isolated $ZnCl_4$ tetrahedra, Cl atoms) which is responsible for the two different groups. In all these structures, the aliphatic chains always tend to organize in the most efficient way. This is accomplished when each chain is in the all-trans conformation (C-C torsion angle of 180°) and lies parallel to the others. This direction tends to be perpendicular to the layers but varies slightly according to the type of counter ion layer. A single kink (C-C torsion angle of ± 60°) on all or part of the chains must be introduced to accommodate the periodicities of the two types of layers. The kink is found near the ammonium end of the chain between the first and second C-atoms or the next C-C pair (fig. 2). In a few cases, exemplified by C14Zn, the adjustement can be reach without kinks by letting the torsion angles to deviate from the all-trans conformation by up to 10°.

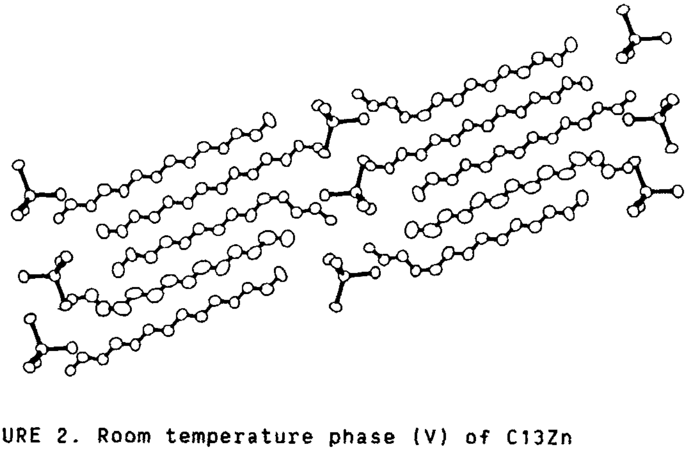

FIGURE 2. Room temperature phase (V) of C13Zn

The structure of the room temperature phase of C13Zn (fig.

2) presents another interesting feature of the packing. Among the four crystallographically independent chains, one has systematically higher thermal coefficients than the other three. This chain is disordered and the structural analysis shows indeed a superposition of two chains conformation which corresponds to the symmetric values $\pm \sigma$ of the torsion angle about the second and third C atoms. Thus, each single organic layer can be divided into zones of ordered chains which alternate with zones of less ordered chains. This feature seems to be preferred instead of distributing uniformously the disorder within the layer. Packing considerations of the aliphatic chains are facilitated by the introduction of the p-cell. Idealizing the central part of the aliphatic layer, i.e. the part which is most distant from the extremities of the chains, it is possible to find the translation periods of the array of carbon atoms which should be similar to paraffins for sufficiently large n.

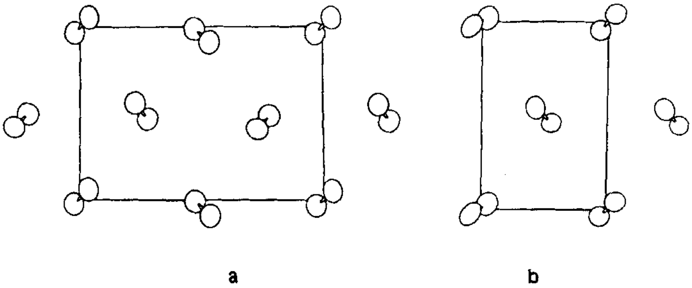

FIGURE 3. p-cells of the series CnZn

Fig. 3 shows the two types of p-cell found in the series CnZn. The type described in fig. 3a is found for even number of carbon atoms and the other type for odd number of

C-atoms. The difference in the p-cell is the cause of the thermal behaviour observed in the series[3] where the number of phase transitions is systematically higher for odd-number of C-atoms.

STRUCTURAL ASPECTS OF THE PHASE TRANSITIONS

All these structures are subjected to numerous phase transitions involving variations of the chain conformations. C13Zn for example shows up to four structural transitions in a temperature interval of 70° degrees. Table I lists the phases along with the thermal characteristics and space group symetry [3-4]

TABLE I. Characteristics of the C13Zn phases.

V	------	IV	------	III	-----	II	----	I	phases
	304		308		315		369		tr. temp[K]
		10			.95		47.5		ΔH [kJ/mol]
		33.5			2.9		131		ΔS [J/mol.K]
$P12_11$	--	$P112_1/a$	--	$P2_111$	--	$Pn2_1a$	--	$Pnma$	Sp. group.

Phases II to V have been determined by single crystal X-ray diffraction along with phase V' which is stable at room temperature after a heating cycle. The transition V to IV is of particular interest due to the disappearance of all kinks with increasing temperature. A comparison between phase IV represented in fig. 4 and phase V (fig. 2) shows how the chains accomodate the all-trans conformation by bending slightly their axis towards the ammonium end. This

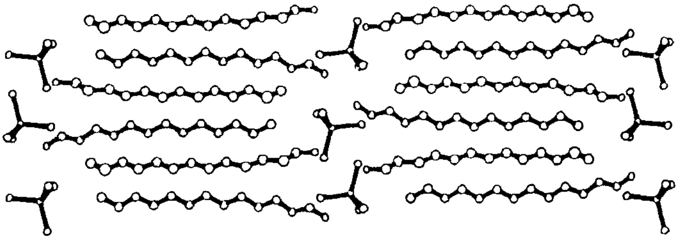

FIGURE 4. Phase IV of C13Zn at 32°C.

transition is accompanied with a reorientation of the chain axis by approximately 20 degrees in a direction perpendicular to the layer. Transition IV to III shows the appearance of disordered C-atoms near the ammonium end which can be interpreted as a coexistence of domains with different chain conformations, partly in the all-trans state the rest with kinks. This transition is also accompanied with a change in the monoclinic axis (c to a) which must be interpreted as a relative displacement of the chains under a shear strain. The disappearance of the metastable room temperature phase V on cooling results from the relative shifts of the chains during the high temperature transitions. Obviously, phase V' is more stable with three chains out of four in the all-trans conformation instead of the 2/2 ratio observed in phase V.

Among the CnM containing non-intercalated n-alkylammonium ions, the manyfold of realized structures and mechanisms is overwhelming. In the series C8Cd to C14Cd, at least three different structural types and five different schemes of phase transitions are observed. The number of transitions varies between two and four and is independent of n. Metastable phases and continuous transitions extending over a large temperature interval could also detected.

C10Cd is the only example of type c (fig. 1) known so far[5]. In the room temperature phase there are two independent chains, each with a kink near the nitrogen atom. The phase is metastable as may be concluded from the difference in the total transition enthalpies upon heating and cooling. In this transformation, pairs of symmetry equivalent chains become independent, one by shifting upwards the C-C torsion angles. The next transition is characterized by partial chain melting and symmetrization of the two ammonium-groups labelled A and in B in figure 5. In addition, parts or the whole of the chains isomerize around the C-C bonds normal to the layer producing thus a slight increase in the separation of the layers.

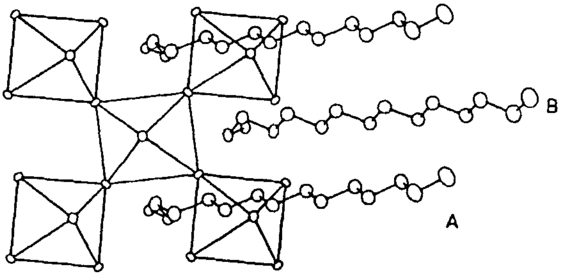

FIGURE 5. View of C10Cd perpendicular to the layer (RT phase)

The room temperature phase of C10Cu[6] adopts the structure represented in fig. 1b. Among the four independent chains, three are in the all-trans conformation whereas the fourth has one kink. The number of independent chains reduces to two upon heating up to the main transition at 30°C. In the DSC, this effect manifests itself as a faint bulging of the baseline. The main transition is almost unanimously alleged to a partial melting of the chains.

TRANSITION FROM INTERCALATED TO NON-INTERCALATED TYPE

Having described the various types of packing found in our models, one could ask about the existence of transition from one type to the other. Indeed, the series CnCl represents such an example where for large values of n ($n \geqslant 10$), an intercalation of chains is observed whereas for smaller values of n, structures with non-intercalated chains are observed[7]. An interesting feature of C10Cl concerns the sequence of phases observed by increasing temperature which can be related to the sequence of room temperature structures by decreasing the value of n : for example, the RT structure of C9Cl corresponds to the first HT phase of C10Cl. The first transition observed in C10Cl is the most prominent ($\Delta H \sim 20$ kJ/mole) and of a reconstructive nature which involves the separation of the chains from type a to b. The subsequent transitions are of the order-disorder type and accompanied by a contraction of the layer separation. The first transition is brought about by a steady increase of the chain diameter due to ever increasing torsional vibrations of the methylene groups. Upon reaching the temperature of transition, a new hydrogen-bonding scheme must be formed providing more space for the chains. The next transitions involves a complete isomerization of the chains around than vertical C-C bonds and a dynamical disordering of the ammonium groups between four equivalent positions.

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