Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Spectroscopic Study of the Structural Phase Transitions in Calcium Tetradecanoate

M. Rey-lafon [a] & A. Tazi Hemlda [a b]

[a] Laboratoire de Spectroscopie Moléculaire et Cristalline (URA 124-CNRS), Université de Bordeaux I, 351 Cours de la Libération, 33405, Talence, Cedex, France

[b] UniversitC de Casablanca I, Maroc

Version of record first published: 24 Sep 2006.

To cite this article: M. Rey-lafon & A. Tazi Hemlda (1991): Spectroscopic Study of the Structural Phase Transitions in Calcium Tetradecanoate, Molecular Crystals and Liquid Crystals, 197:1, 67-81

To link to this article: http://dx.doi.org/10.1080/00268949108029703

Mol. Cryst. Liq. Cryst., 1991, Vol. 197, pp. 67–81
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Spectroscopic Study of the Structural Phase Transitions in Calcium Tetradecanoate

M. REY-LAFON and A. TAZI HEMIDA†

Laboratoire de Spectroscopie Moléculaire et Cristalline (URA 124-CNRS), Université de Bordeaux I, 351 Cours de la Libération, 33405 Talence Cedex, France

(Received June 28, 1990; in final form October 16, 1990)

From a vibrational spectroscopic study of calcium tetradecanoate, descriptions of the molecular structures in the solid and mesomorphic phases and of their thermotropic interconversions are proposed. Phase A, stable at room temperature, crystallizes in an ordered lamellar structure. The solid A-solid B phase change, near 100°C, implies the onset of motions of the whole molecule, entailing a modification of the crystal lattice. The transitions solid B-mesophase C (near 113°C) and between mesophases C and D (130°C) involve a rapid disordering of the hydrocarbon layers through the formation of conformational defects (GG forms, kinks and GTG sequences). These defects induce the breaking of sheets into discs situated in equidistant planes and a progressive decreasing of the intersheet distance when raising the temperature and passing from phase C to phase D and phase E (stable between 160 and 180°C). The structure of the polar layers also changes through the phase transitions, so as to allow the formation of cylinders in phase F observed above 180°C.

Keywords: calcium tetradecanoate, spectroscopic studies of . . ., phase transitions for . . .

INTRODUCTION

The melting behavior of compounds constituted of long aliphatic chains with an ionic end group has been the subject of a great number of papers. These compounds crystallize in layer structures similar to those of n-alkanes, but an extra-stabilization of the layers is provided by long range Coulomb forces. In n-alkylammonium chlorides, for instance, layers of hydrogen bonded N and Cl atoms are sandwiched between alkylammonium cations. Solid-solid phase transitions lead to a high temperature phase in which the aliphatic chains are disordered; the ammonium groups perform jumps between several equivalent potential wells and only short range order exists.[1,2,3] Mesomorphic phases have been evidenced before final melting.[4] Fatty acid salts which contain an organic anion are expected to present a comparable behavior. Numerous studies using X-ray diffraction, DSC and optical measurements have shown that they possess complex sequences of phase transitions including the

† Present address: Université de Casablanca I, Maroc.

formation of mesophases. However, except for some potassium, sodium and copper salts in the solid state, no accurate description of the molecular structure in the different phases has been published and the mechanisms of the transitions are not understood. Further researches are thus justified, not only because these compounds possess important practical properties, but also because they constitute very useful model systems for biological membranes.

Calcium tetradecanoate, $[CH_3(CH_2)_{12}COO]_2Ca$, has been the subject of a careful X-ray diffraction study which allowed determination of the structural characteristics of the various phases and establishment of the phase diagram (Figure 1).[5] Six phases are observed prior to the decomposition temperature: A and B are solid, C, D, E and F are mesomorphic.

In room temperature phase A, observed until about 100–110°C, the carboxylate groups are located in parallel and equidistant planes separated by double sheets of alkyl chains perpendicular to the layers. The chains are assumed to be in the all-*trans*-conformation as in solid n-paraffins. The structure of phase B is also lamellar, and the chains are still perpendicular to the layer planes. The packing of the molecules seems to have a high symmetry which suggests a reorientational motion about their long axis and a hexagonal lattice. In mesophases C, D and E, the molecules, associated through their polar ends, form discs which are situated in equidistant planes (phase C), at the nodes of a *C*-base-centered orthorhombic

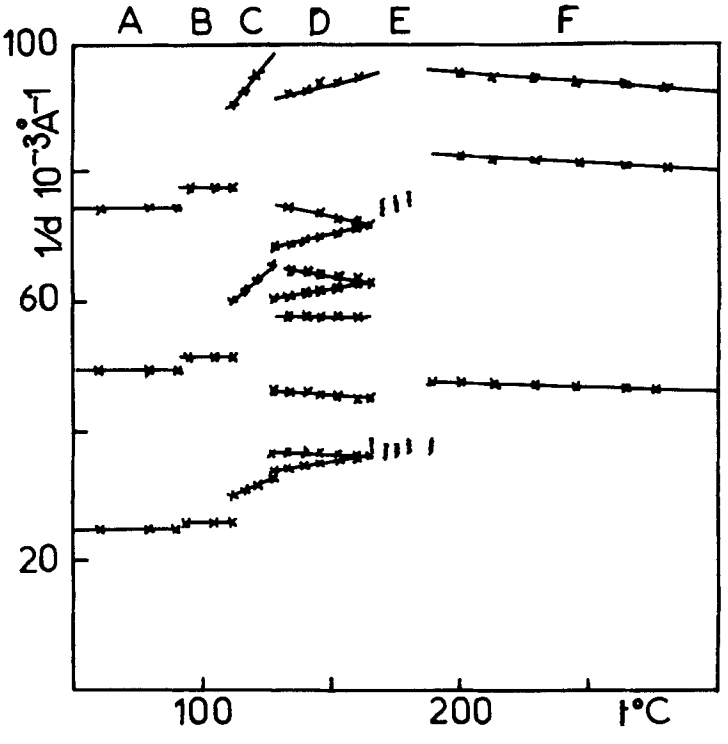

FIGURE 1 Phase diagram obtained from X-ray measurements.[5]

lattice (phase D) or in planes which are no longer equidistant (phase E). Disordered aliphatic chains fill the space between the discs. Mesophase F is constituted of parallel infinite cylinders located at the nodes of a hexagonal bidimensional lattice; the cylinders are formed by the polar heads surrounded by the aliphatic chains in the disordered state.

The studies carried out so far lead to a model of the structure of the molecular aggregates and their evolution through the phase transitions. However, the description of the changes at the molecular level, in terms of the chain conformation, the geometry of the carboxylate end and the structure of the polar layers remains very vague, despite a Raman study of some calcium salts.[6] The aim of this work was to try to elucidate some of the above problems.

EXPERIMENTAL PART

Calcium tetradecanoate was prepared following the method described by Spegt *et al.*[5] and thoroughly dried at 110°C under vacuum in order to destroy the hydrates. DSC measurements‡ have shown that the material gives the same sequence of transitions as that observed by X-ray diffraction.[5]

Phase B was obtained by heating form A between 110 and 112°C. Three hours' heating at 130°C were necessary to obtain phase C. Transitions C → D, D → E and E → F were easily obtained. The temperatures were stable within 1°C.

The infrared spectra were obtained using homogeneous samples made by thoroughly mixing the finely powdered material with a very small quantity of nujol or fluorolube. In order to be precise about the real phase we had for each recorded spectrum, we verified that the spectra of the mulls and of the powder are similar at each temperature, over the whole range 20–200°C. Moreover the DSC diagram of a nujol mull shows the same transition temperatures (within 2°C) and enthalpies as that of the powder, in the solid state and at the transition solid-mesomorphic state. The mulls were squeezed between CsI or polyethylene windows and the spectra were recorded with a grating spectrometer Perkin-Elmer 983 G (resolution 3 cm^{-1}) or with a FTIR Bruker 113 V (resolution 1 cm^{-1}) for the mid infrared; for wavenumbers below 200 cm^{-1}, we used a FTIR Nicolet 20 F (resolution 4 cm^{-1}).

Raman spectra of powdered samples were obtained using a Coderg T 800 spectrometer equipped with a triple monochromator. The spectral slit widths varied from 1 to 3 cm^{-1}. The 514.5 nm line of Spectra-Physics Ar ion lasers (models 165 and 171) was used for excitation, with a power of 200 mW.

STUDY OF THE ORDERED SOLID PHASE

To facilitate the interpretation of the spectrum of phase A, in particular the assignment of the carboxylate deformations, we performed a normal coordinate treatment, using the Wilson method and a valence force field. A transferable,

‡ We thank Professor C. Destrade of the Centre de Recherche Paul Pascal for these measurements.

approximate force field was obtained from the study of form A (stable at room temperature) of potassium decanoate. Indeed, the structure of this crystal has been determined by X-ray diffraction[7]: the chains are in the all-*trans*-conformation; the zig-zag skeleton and the carboxylate group are nearly coplanar. We recorded the infrared and Raman spectra of potassium decanoate and performed the normal mode calculation, assuming the tetrahedral geometry, with C—C, C—H and C—O bond lengths equal to 1.54, 1.093 and 1.26 Å, respectively; the angles CCO and OCO were taken as 120°. For the hydrocarbon part, the force field used was that derived by Snyder for n-alkanes.[8] For the CH_2-COO group, we successively tried the force constants proposed for CH_3CH_2COONa,[9] for the potassium salts[10] and for glycine and glycylglycine.[11] The latter gave the best agreement with the experimental frequencies in the whole spectral domain, as shown in Table I for the carboxylate vibrations. We thus chose these force constants for an approximate calculation of the normal modes of calcium tetradecanoate.

Conformation of the Hydrocarbon Chains

As crystallographic results suggest that the chains are in extended conformation, their spectra are usefully compared with those of solid n-alkanes.

The infrared spectrum presents the progression bands due to non-localized modes of all-*trans*-chains, the frequency of which is characteristic of both length and configuration of the chains (Figure 2). The intense Raman bands at 1130 and 1064 cm^{-1} respectively, correspond to the in-phase and out-of-phase carbon-carbon stretching of an infinite n-alkyl chain (Figure 3). The longitudinal acoustic mode (LAM) has been assigned to a line of medium intensity at 188 cm^{-1}[6b] (Figure 4). This wavenumber is higher than the LAM frequency for n-alkanes with 14 or 15 carbon atoms (164 and 153 cm^{-1} respectively)[12] and higher than the calculated value, 143 cm^{-1}, which takes into account the mass effect of the oxygen atoms. However, the electrostatic interactions between $—COO^-$ anions and Ca^{2+} cations, and the structure of the polar layers are not considered, though they probably have a great influence on the LAM frequency. Assignment of the LAM mode in relation

TABLE I

Comparison of experimental and calculated wavenumbers (cm^{-1}) of the COO group in potassium decanoate, using different force fields

	Kakihana *et al.*[9]	Cass* [10]	Destrade *et al.*[11]	Experiment
υ_a(COO)	1587(0.85)	1552(0.86)	1568(1.04)	1564
υ_s(COO)	1481(0.51)	1369(0.75)	1407(0.5)	1416
δ(COO)	704(0.51)	697(0.65)	690(0.47)	697
		816(0.12); 766(0.13)		
r(COO)	661(0.84)	731(0.11); 711(0.1)	680(0.65)	676
		700(0.6)		
γ(COO)	642(0.4)	538(0.31)	599(0.52)	585

Figures between brackets correspond to Potential Energy Distribution of the vibrational mode (100 $Li^2_{ik}F_{ii}/\lambda_k$).

* We have chosen the Cass force field which gives the best agreement between observed and calculated frequencies of potassium pentanoate.

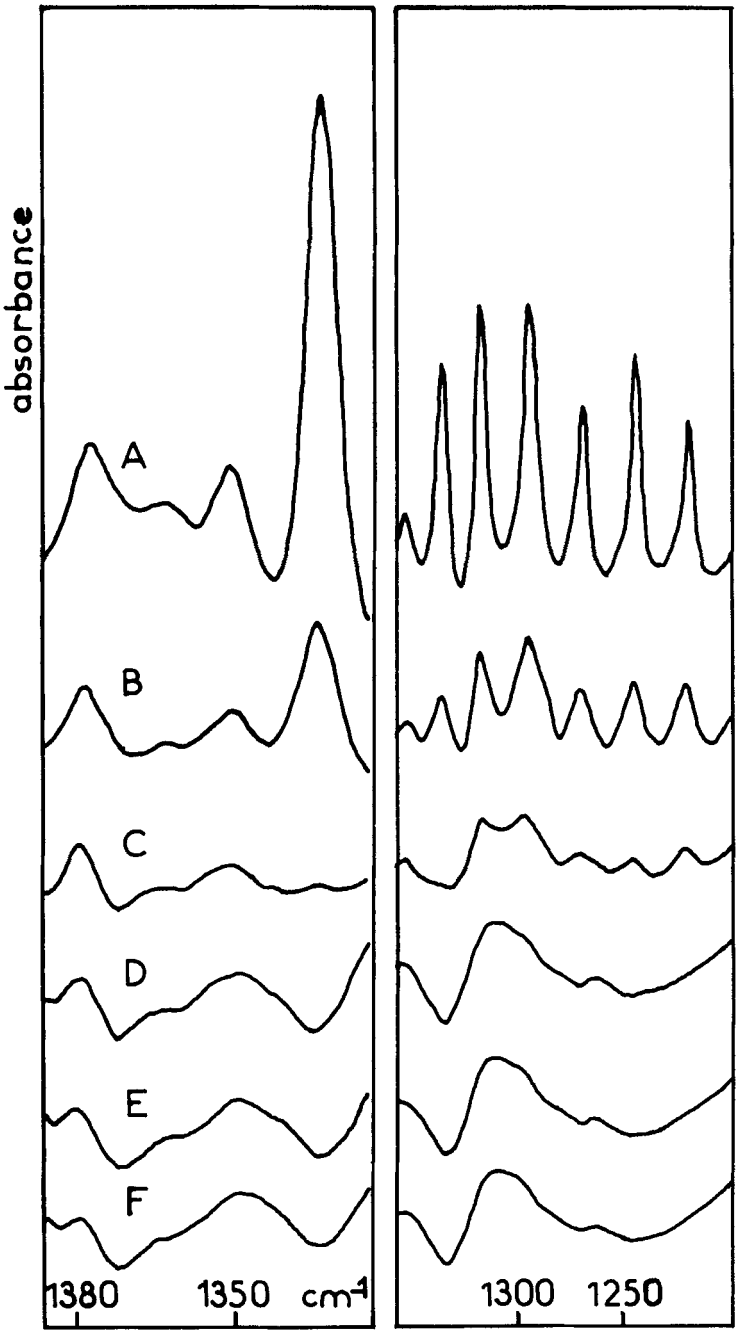

FIGURE 2 Temperature dependence of the infrared spectrum between 1200 and 1380 cm^{-1}. Phase A at 25°C; B at 110°C; C at 118°C; D at 138°C; E at 175°C; F at 195°C.

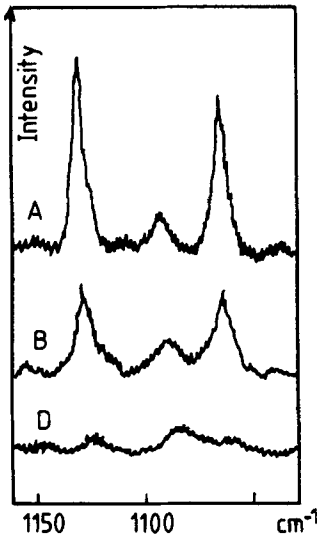

FIGURE 3 Temperature dependence of the Raman spectrum between 1030 and 1160 cm^{-1}. Phase A at 25°C, B at 110°C; D at 130°C.

to the above factors needs further study and will be discussed in a subsequent paper.

Localized modes, corresponding to vibrations of a limited part of the chains, have a frequency which depends on the local conformation only. The $r(CH_3)$ Raman frequency at 892 cm^{-1} corresponds to a *trans*-geometry in the vicinity of the methyl end. The $\delta_s(CH_3)$ transition observed at 1379 cm^{-1} in the infrared is also a localized vibration; this frequency is higher than that found for solid n-alkanes, which indicates that chain interactions at the methyl end are weaker.[13]

In the Raman spectrum, the CH stretching domain presents well defined maxima; those at 2850 and 2885 cm^{-1} are attributed to $\upsilon_s(CH_2)$ and $\upsilon_a(CH_2)$, respectively. The maximum near 2962 cm^{-1} belongs to the methyl group. The other maxima and the broad diffusion between 2850 and 3000 cm^{-1} are characteristic of extended methylene chains and due to Fermi resonances between the $\upsilon_s(CH_2)$ and the quasi-continuum of the bending progression band overtones.[14] The line at 1417 cm^{-1} is assigned to the most symmetrical component of a splitting of the $\delta(CH_2)$ vibration due to the crystalline field. The two maxima at 1443 and 1463 cm^{-1} correspond to Fermi resonances between the other component of the crystal field splitting and a combination of $r(CH_2)$ transitions. Other ill defined scattering bands also are due to Fermi resonances with overtones and combinations of $r(CH_2)$, and to the methyl antisymmetrical deformations[14] (Figure 5).

Conformation in the Vicinity of the Carboxylate Groups

The carboxylate deformation $\delta(COO)$ and the in-plane and out-of-plane rocking modes, $r(COO)$ and $\gamma(COO)$ are assigned to absorptions at 697, 600 and 668 cm^{-1} respectively, according to the results of the normal mode treatment, with the

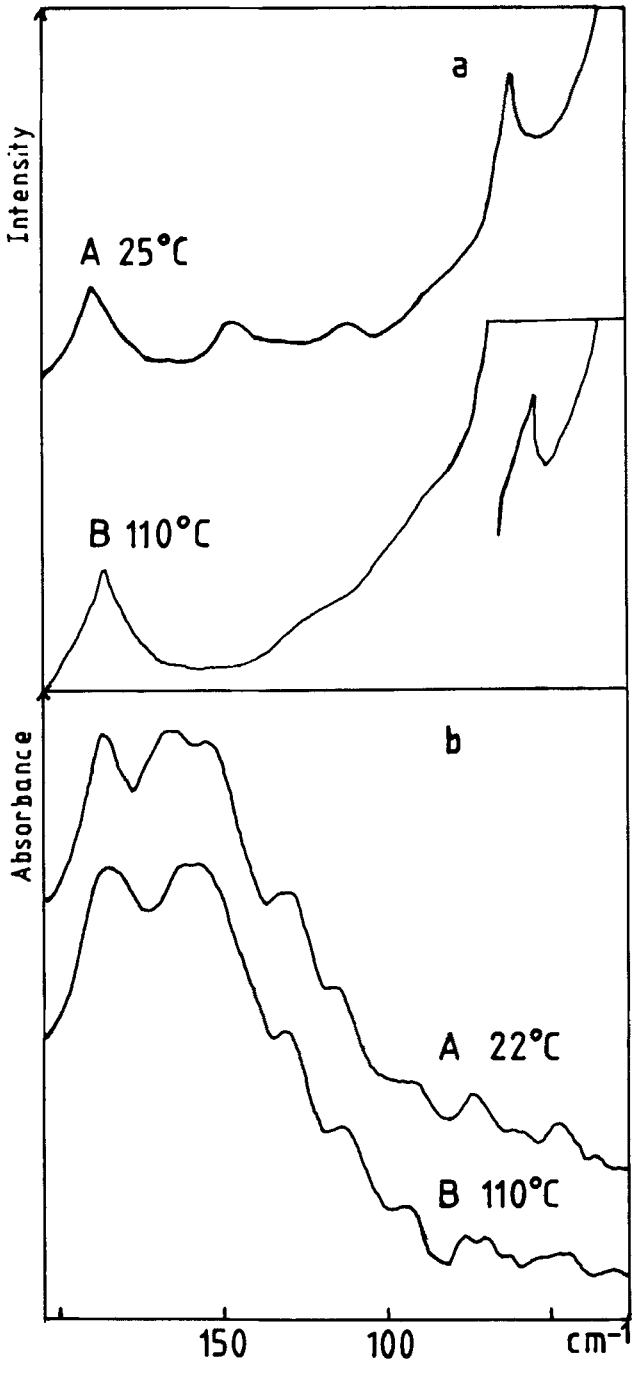

FIGURE 4 Infrared and Raman spectra below 200 cm^{-1}.

TABLE II

Calculated frequencies (wavenumbers) of the carboxylate group as a function of the dihedral angle ψ

ψ	υ_a(COO)	υ_s(COO)	δ(COO)	γ(COO)	r(COO)
0°	1570(1.04)	1408(0.85)	690(0.47)	682(0.69)	600(0.51)
10°	1570(1.04)	1408(0.85)	697(0.28)	677(0.43)	599(0.51)
20°	1570(1.04)	1408(0.85)	672(0.28)	672(0.32)	595(0.53)
30°	1571(1.04)	1408(0.85)	668(0.33)	668(0.26)	590(0.57)
40°	1571(1.03)	1408(0.85)	666(0.36)	738(0.33)	584(0.61)
50°	1572(1.03)	1408(0.85)	664(0.39)	755(0.40)	578(0.66)
60°	1573(1.03)	1408(0.85)	663(0.40)	765(0.48)	573(0.71)
70°	1574(1.03)	1408(0.85)	662(0.40)	773(0.50)	569(0.75)
80°	1575(1.02)	1408(0.85)	661(0.41)	780(0.25) 777(0.26)	566(0.78)
90°	1577(1.02)	1408(0.85)	660(0.40)	780(0.51)	565(0.76)

Figures between brackets correspond to Potential Energy Distribution of the vibrational mode (100 $Li^2_{ik}F_{ii}/\lambda_k$).

Only the frequency with the largest PED is given.

assumption that the carbon skeleton and the COO group are coplanar ($\psi = 0$) (form I) as in potassium decanoate form A, or about coplanar (ψ up to 10–15°) (Table II). An absorption band at 656 cm^{-1} is not attributed. When raising the temperature, the intensity of the bands assigned to form I diminishes; the absorption at 656 cm^{-1} and a maximum at 758 cm^{-1} become more intense, while the progression bands weaken all along the spectrum (Figure 6). These features suggest that the two peaks at 656 and 758 cm^{-1} belong to a structure with a different geometry at the carboxylate end (form II). Results of normal mode calculations carried out when varying the dihedral angle ψ between 0 and 90° are given in Table II. A ψ angle of either 50–60° or 90° leads to a good agreement between the calculated and observed frequencies. Semi-empirical calculations for an isolated tetradecanoate ion show a very flat energy minimum near 80–90° (MNDO, MNDO/3, PM3) or 40–50° (AM1); the maximum of the energy difference is less than 1 Kcal $mole^{-1}$ which indicates a very easy rotation around the C_1-C_2 bond. The higher content of form I in phase A is due to the interactions with the Ca^{2+} cations and to the crystalline structure constraints.

Structure of the Polar Layer

Crystal field splittings of $\delta(CH_2)$ (1473–1463 cm^{-1}) and $r(CH_2)$ (732–719 cm^{-1}) transitions are observed in the infrared spectrum; they are indicative of at least two molecules in the unit cell. The subcell formed by the CH_2 groups of two molecules in a layer is thus orthorhombic as in polyethylene and a number of solid n-alkanes. It has been shown that such a subcell packing implies a monoclinic or orthorhombic crystal structure.[15] As the molecules of calcium tetradecanoate are perpendicular to the layers, from X-ray results, the lattice symmetry is more likely orthorhombic.

A similar splitting of the $\delta(CH_2)$ vibration has been observed in the spectrum of lead and cadmium stearates on bulk and multilayer samples.[16] The υ_a(COO)

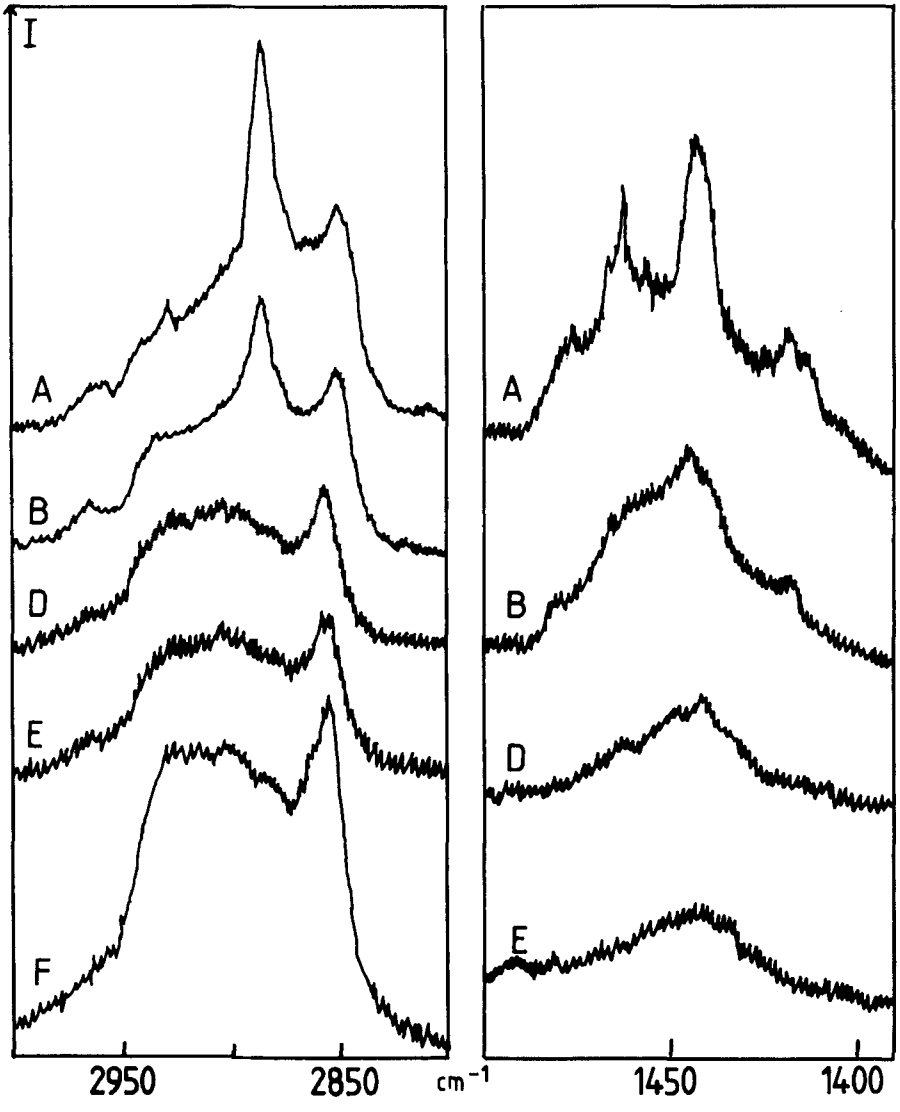

FIGURE 5 Temperature dependence of the Raman spectrum in the CH_2 stretching and bending domains. Phase A at 25°C; B at 110°C; D at 130°C; E at 160°C; F at 200°C.

band of the lead salt presents two components at 1541–1513 cm^{-1}; a broad unresolved absorption corresponds to this in the case of cadmium stearate. These compounds form solid solutions with stearic acid of form C, the structure of which has been described.[17] From the analysis of the spectra of the stearates and stearic acid form C, Vogel *et al.* proposed a structure in which the polar groups form cyclic dimers (Figure 7a); the latter are packed in a monoclinic lattice.[16] This conclusion agrees with the structure proposed for tridimensional crystals of lead stearate from electron microscopy measurements.[18]

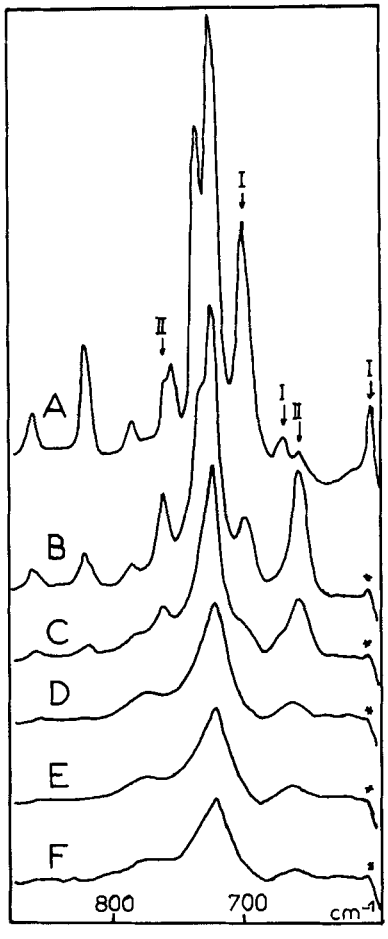

FIGURE 6 Temperature dependence of the infrared spectrum in the 600–875 cm^{-1} range. See Figure 2 caption. * Artefact due to a change of grating.

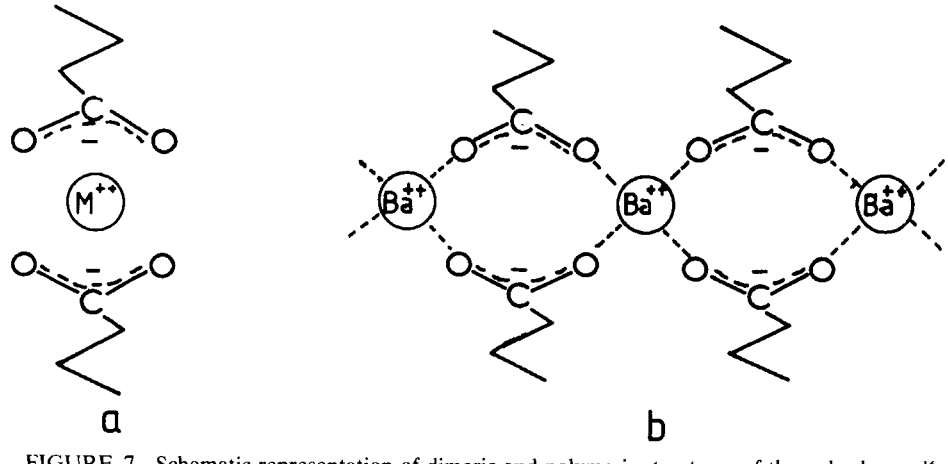

FIGURE 7 Schematic representation of dimeric and polymeric structures of the polar layers.[16]

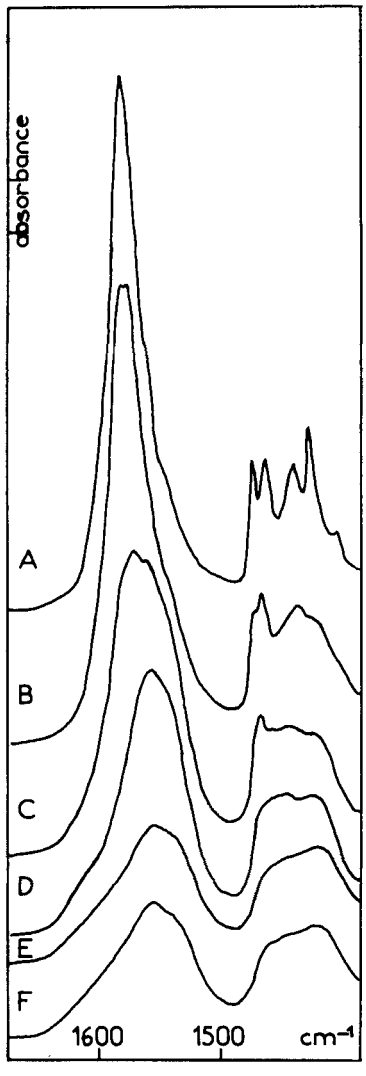

FIGURE 8 Temperature dependence of the infrared spectrum in the 1400–1650 cm^{-1} range. See Figure 2 caption.

The case of barium stearate is different, since the $\upsilon_a(COO)$ and $\delta(CH_2)$ modes are assigned to single bands at 1509 and 1470 cm^{-1}, respectively. This suggests a triclinic packing of the chains. This different behavior is explained by the larger radius of the Ba^{++} cation (r_{Ba2+} = 1.34 Å, r_{Pb2+} = 1.2 Å, r_{Cd2+} = 0.97 Å) which makes the formation of a dimer more difficult. This cation would be surrounded in the same plane by four oxygen atoms of four carboxyl groups, leading to a "polymer" type structure (Figure 7b).[16]

The spectrum of calcium tetradecanoate resembles that of cadmium stearate since the $\upsilon_a(COO)$ band is broad, but does not present a resolved splitting, the

shoulders observed at 1560 and 1545 cm^{-1} being probably due to overtones or combinations (Figure 8). As the ionic radius of Ca^{2+} (0.99 Å) is close to that of Cd^{2+}, it seems reasonable to attribute the same structure to the polar layers of the two crystals. Unfortunately, we were unable to observe the Raman lines corresponding to the carboxylate stretching modes which could have allowed confirmation of this conclusion.

The stretching and deformation transitions of the dimer are expected at low wavenumbers. The spectra below 200 cm^{-1} are displayed in Figure 4. Except for the band at 188 cm^{-1}, which corresponds to an internal mode, the infrared and Raman frequencies do not coincide. This result supports the hypothesis of a centrosymmetric cyclic dimer.

This study gives evidence for the existence of inter- and intra-molecular coupling in *trans*-planar chains and of two conformations in the vicinity of the carboxylate group. The polar layer seems to be constituted of cyclic dimers.

CHANGES IN THE VIBRATIONAL SPECTRA OF THE DISORDERED PHASES

Conformation of the Alkyl Chains

The infrared spectrum of the hydrocarbon chain in phase B is not very different from that observed in phase A, except for the intensity of the progression bands which is weaker. It does not possess any absorption that is characteristic of the specific sequences of *gauche* (G) and *trans* (T) bonds which are observed in the high temperature solid phase of the odd n-alkanes.[8] In the CH bending domain of the Raman spectrum, the peak intensity at 1465 cm^{-1} diminishes with regard to the methyl transition at 1456 cm^{-1}. The $\upsilon_a(CH_2)$ band at 2885 cm^{-1} broadens and the peak intensity near 2930 cm^{-1} increases with respect to the $\upsilon_s(CH_2)$ line at 2850 cm^{-1}. These features and a very weak scattering wing near 1078 cm^{-1} reveal the occurrence of some *gauche*-bonds. However, the C—C stretching bands of all-*trans*-chains are still intense and the band at 188 cm^{-1} is observed. The aliphatic chains thus are mainly in an extended conformation, though some *gauche* defects are present. The disorder in phase B seems to be principally due to angular fluctuations around the molecular axis, maintaining a linear shape.

In mesophase C, the intensity of the progression bands strongly decreases and new bands appear: a broad one, near 1310 cm^{-1}, on which the progression peaks at 1315 and 1295 cm^{-1} are still observed, a maximum at 1366 cm^{-1}, and two shoulders at 1354 and 1343 cm^{-1}. In n-alkanes,[8] the latter two absorptions have been respectively assigned to GG sequences and to G bonds in the vicinity of the methyl end; those at 1366 and 1310 cm^{-1} are characteristic of GTG and GTG′ structures. They are indicative of the same types of defects in calcium tetradecanoate, since it has been shown that the presence of a highly polar end group induces only slight shifts of these defect frequencies.[20]

Infrared and Raman spectra of phase D at 138°C no longer show characteristic features of extended chains. Progression bands overlap and tend to form a continuous background; the maxima due to defects of the type GTG or GTG′, GG

sequences and G forms at the methyl end are intense. The limiting $|k| = 0$ mode lines disappear, the intensity of the shoulder at 1465 cm^{-1} decreases. The $\upsilon_a(CH_2)$ band merges into a broad scattering near 2900 cm^{-1} and the $\upsilon_s(CH_2)$ frequency is shifted by 5 cm^{-1} towards higher values, which indicates a diminution of the length of the *trans*-sequences.[21] The conformational disorder thus is very important in phase D.

It must be noticed that the disorder increases when the temperature is raised within phase D. At 160°C, indeed, the line at 2885 cm^{-1} cannot be distinguished from the broad scattering background near 2900 cm^{-1}; however the ratio I_{2930}/I_{2850} is not changed, a result which suggests that this increase of disorder is mainly due to an increased mobility of the chains.

Phases E and F possess spectra very similar to those of phase D; the peaks assigned to defects are slightly more intense.

Conformation in the Vicinity of the Carboxylate Group

Important modifications of the infrared spectrum are observed in the spectral domain 600–800 cm^{-1}, in phase B. The bands at 656 and 758 cm^{-1} are intense, while the absorptions assigned to form I are no longer observed, except the $\delta(COO)$ peak whose intensity has strongly diminished. Form II is thus preponderant.

This evolution continues in phase C where form I practically has disappeared. In the other mesophases, broad flat absorptions suggest fluctuations of the dihedral angle ψ.

Structure of the Polar Layer

The structure of dimeric type persists in phase B, since the infrared bands assigned to $\delta(CH_2)$ and $\upsilon_a(COO)$ and those which can be observed below 200 cm^{-1} are about the same as in phase A. The Raman signals at 188 and 60 cm^{-1} are still present but other lines are not observed. The strong broadening of the Rayleigh line is consistent with a dynamical disorder in phase B.

In phase C, the $\delta(CH_2)$ transition is not split, the band corresponding to $\upsilon_a(COO)$ is shifted to 1571 cm^{-1}. The frequency shift is more important in phases D, E and F since the peak maximum is at 1554 cm^{-1}. This strong frequency modification indicates a change in the surroundings of the carboxylate group. This remark is consistent with the fact that cyclic dimeric structures are impossible in the cylinders of phase F.

Intermolecular Interactions

Splittings due to the coupling of the molecular vibrations in the unit cell are still observed in the infrared and the Raman spectra of solid phase B, but the frequency differences between the components are less important than in phase A. This effect, which indicates that the intermolecular interactions are weaker, is more important for the rocking $r(CH_2)$ band. The high frequency component is the most affected: its intensity is reduced and its frequency decreases; the other component broadens and moves to a slightly higher frequency. Similar features have been observed and discussed for the high temperature solid phase of the odd n-alkanes ($17 \leqq n \leqq$

27).[19] They can be due either to a modification of the crystal structure through an expansion of the parameter cells (static factor), or to dynamical factors associated with rotational/twisting motions about the chain axis; in the latter case, the crystal structure tends to attain a hexagonal symmetry. In the case of calcium tetradecanoate phase B, the spectroscopic evidence shows the existence of motions of the whole molecule; this suggests that the crystal lattice tends to become hexagonal in phase B.

CONCLUSION

This spectroscopic study thus provides a picture of the molecular structures in the solid and mesomorphic phases of calcium tetradecanoate. Phase A is an ordered solid in which the molecules have little mobility and intermolecular interactions are noticeable. The aliphatic chains are entirely extended and two geometries in the vicinity of the carboxylate group are stabilized. The CH_2 groups are packed in an orthorhombic subcell which most likely corresponds to an orthorhombic crystal modification. The polar layers seem to be constituted of cyclic dimers.

Phase B presents a dynamical disorder due to the onset of chain motions and a weakening of the intermolecular interactions. The chains essentially are in an extended conformation, though they admit some *gauche* forms. The proportion of form I, in which the carbon skeleton and the COO group are about coplanar, strongly diminishes. The structure of the polar layer is similar to that of phase A, but the spectroscopic evidence is consistent with a different lattice tending to a hexagonal symmetry.

An important conformational disorder characterizes mesophase C; the chains possess several conformations comprising G bonds, such as GTG or GTG′ defects, GG sequences and G forms at the methyl end. However, a noticeable proportion of extended chains is still present. The geometry I no longer exists and the surroundings of the carboxylate group inside the polar layer are modified.

The conformational disorder is even greater in phases D, E and F where extended chains are no longer observed. The chain mobility increases with temperature and includes the bonds near the carboxylate end. The spectra suggest that the structure of the polar layer is the same in phases D, E and F and is not of dimeric type, which is consistent with the cylinder structure of phase F.

By combining the present conclusions with previous crystallographic results,[5] a picture of the disordering process in calcium tetradecanoate is obtained: upon raising the temperature, molecular motions and some *gauche* rotations become activated, the intermolecular interactions weaken and the chains tend to form a hexagonal or pseudo-hexagonal lattice. The angle between the COO group and the carbon skeleton varies, but the polar groups remain strongly bound in the high temperature solid phase.

The conformational disorder in the mesophases produces a lateral expansion of the hydrocarbon parts which induces the breaking of the sheets and the formation of discs. As the temperature increases, the chains partially diverge which explains

the decrease of the intersheet distances in phases C and D. At the same time, the dimeric structure of the polar layers is lost in favor of a different arrangement of the polar salt group allowing the formation of cylinders.

Acknowledgment

The authors are grateful to Prof. C. Destrade for helpful discussions, to Dr. B. Duguay for the MNDO and AM1 calculations and to Dr. C. Sourisseau for critically reading the text. A. Roubineau, R. Cavagnat and J. C. Cornut are cordially thanked for their technical assistance.

References

1. R. Kind, R. Blinc, H. Arend, P. Muralt, J. Slak, G. Chapuis, K. J. Schenk and B. Zeks, *Phys. Rev.*, **A26**, 1816 (1982).
2. K. J. Schenk, C. A. Ogle, G. Chapuis, R. Cavagnat, A. Jokic and M. Rey-Lafon, *J. Phys. Chem.*, **93**, 5040 (1989).
3. K. J. Schenk, G. Chapuis, D. Swarzenbach, C. A. Ogle, J. C. Cornut and M. Rey-Lafon, to be published.
4. V. Busico, P. Corradini and M. Vacatello, *J. Phys. Chem.*, **86**, 1033 (1982); V. Busico, P. Cernicchiaro, P. Corradini and M. Vacatello, *J. Phys. Chem.*, **87**, 1631 (1983).
5. P. A. Spegt and A. E. Skoulios, *Acta Cryst.*, **17**, 198 (1964).
6. (a) R. Faiman and D. A. Long, *J. Raman Spectr.*, **3**, 371 (1975); (b) R. Faiman, G. Vergoten, Y. Moschetto and D. A. Long, *Proc. 5th Int. Conf. on Raman Spectroscopy*, Freiburg (1976), p. 544.
7. E. L. V. Lewis and T. R. Lomer, *Acta Cryst.*, **B25**, 702 (1969).
8. R. G. Snyder, *J. Chem. Phys.*, **47**, 1316 (1967).
9. M. Kakihana and M. Akiyama, *J. Phys. Chem.*, **91**, 4701 (1987).
10. D. A. Cass, Thesis, University of California, Berkeley (1977).
11. C. Destrade, C. Garrigou-Lagrange and M. T. Forel, *J. Mol. Struct.*, **10**, 203 (1971).
12. J. R. Scherer and R. G. Snyder, *J. Chem. Phys.*, **72**, 5798 (1980).
13. (a) G. Zerbi, R. Magni, M. Gussoni, K. H. Moritz, A. Bigotto and S. Dirlikov, *J. Chem. Phys.*, **75**, 3175 (1981); (b) G. Conti, G. Minoni and G. Zerbi, *J. Mol. Struct.*, **118**, 237 (1984).
14. R. G. Snyder and J. R. Scherer, *J. Chem. Phys.*, **71**, 3221 (1979).
15. R. G. Snyder, *J. Mol. Spectr.*, **4**, 411 (1960); **7**, 116 (1961).
16. C. Vogel, J. Corset and M. Dupeyrat, *J. Chim. Phys.*, **76**, 903 (1979); **76**, 909 (1979).
17. R. F. Holland and J. R. Nielsen, *J. Mol. Struct.*, **9**, 436 (1962).
18. J. F. Stephens and C. Tuck-Lee, *J. Appl. Cryst.*, **2**, 1 (1969).
19. H. L. Casal, H. H. Mantsch, D. G. Cameron and R. G. Snyder, *J. Chem. Phys.*, **77**, 2825 (1982).
20. L. Ricard, M. Rey-Lafon and C. Biran, *J. Phys. Chem.*, **88**, 5614 (1984).
21. L. Ricard, S. Abbate and G. Zerbi, *J. Phys. Chem.*, **89**, 4793 (1985).