ARTICLES

A Vibrational and Structural Study of the Solid–Solid Phase Transitions in C₁₀H₂₁NH₃Cl

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The joint vibrational and structural study of *n*-decylammonium chloride results in a fair description of the solid phases and their interconversions during the thermotropic phase transitions. Phase i (stable below 312 K) crystallizes as a well-ordered, interdigitated layer structure, whereas phases α (stable above 318 K), β (stable between 318 and 316 K), δ (stable between 316 and 302 K), and ϵ (metastable below 302 K) represent intermediate states between a very disordered smectic B and a quite densely packed smectic H. The $i \rightarrow \delta$ transition consists in a reconstructive separation of the *n*-decylammonium chains, whereas the other transitions entail a successive disordering of the organic layers and the polar lattice. Disorder in the aliphatic chains takes the form of chain defects (G forms, GTG sequences, and kinks). Disorder in the polar lattice consists of jumps of the ammonium groups between several equivalent potential wells inside an appropriately distorted tetragonal chlorine pyramid. Only short-range order exists in phase α , whereas there are some intralayer correlations in phases β , δ , and α ; different chain tiltings and packings are realized, however. This difference is also reflected in different molecular motions in phases δ , β , and α .

Introduction

Polymorphism in *n*-decylammonium chloride (C10Cl) has attracted the curiosity and challenged the wits of many a researcher.¹⁻²⁰ The binary phase diagram of this layer compound with water displays an overwhelming number of phases⁶ and mesophases⁴ which are interconnected by intriguing, but elusive thermotropic,^{1,6} lyotropic, and barotropic⁸ transformations. Most of these are known rather sketchily and require further study. A more extensive investigation seems indeed justified, not only because C10Cl is useful as a powerful *model system* for biomembranes,⁶ but also because *n*-alkylammonium chlorides (C*n*Cl) have important *technical applications* as emulsifiers, lubricants, surfactants, detergents,⁹ corrosion inhibitors, soil conditioners, and bactericides.

Between -195 and +130 °C five major solid phases (Figure 1) of C10Cl have been identified and characterized by means of X-ray diffraction and various spectroscopic techniques.^{5,6,8,11-18} Phase i, the stablest state, crystallizes easily and forms a well-ordered, three-dimensional structure¹⁰ (Figure 2a); its properties have been extensively studied and discussed.^{6,8,11} Phases α , β , δ , and ϵ , however, resemble smectic mesophases and are available only as powders. From these it is extremely difficult to extract any structural information since the long basal spacing of layer compounds and the anisotropy of their powders give rise to crowded, fuzzy, and tricky powder diagrams. Fortunately, some insight can be gleaned by analogy with *n*-hexylammonium chloride (C6Cl) and *n*-octylammonium chloride (C8Cl) which crystallize more readily at room temperature.

In this report we shall call two phases, P_1 and P_2 , of *n*-alkyl-ammonium chlorides "isomorphous" if the following conditions hold:

(i)
$$a(\mathbf{P}_1) \approx a(\mathbf{P}_2); \quad \alpha(\mathbf{P}_1) \approx \alpha(\mathbf{P}_2) \approx 90^\circ$$

 $b(\mathbf{P}_1) \approx b(\mathbf{P}_2); \quad \beta(\mathbf{P}_1) \approx \beta(\mathbf{P}_2) \approx 90^\circ$

 $d_{001}(\mathbf{P}_1) \approx d_{001}(\mathbf{P}_2) \mod (1.2 \text{ Å}); \quad \gamma(\mathbf{P}_1) \approx \gamma(\mathbf{P}_2) \approx 90^{\circ}$

(ii) Consistent (hk0) intensities (i.e., similar p cells²¹) and comparable (00*l*) intensities of P₁ and P₂.

(iii) Similar degree of disorder in P_1 and P_2 (e.g., comparable ¹H NMR second moments).

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(21) The name p cell (instead of subcell) for the unit cell characterizing the finite packing of the aliphatic radicals seems preferable to us; for by using p cell, no confusion with the totally unrelated unit cell of the crystal structure can arise.

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Figure 1. Thermotropic phase transitions between the five major solid phases of C10Cl. The numbers by the arrows indicate transition temperatures [$^{\circ}$ C] as found by X-ray diffraction. (Those in parentheses were obtained from DSC measurements.)

In order to clearly refer to the many phases of C6Cl, C8Cl, and C10Cl mentioned below, a phase will be denoted by its phase label followed by the number of carbon atoms in brackets. α [C8], e.g., will stand for phase α of C8Cl. Whenever a phase is cited without the quantity in brackets it will be one of C10Cl.

All of the transformations between the i, α , β , δ , and ϵ phases have been shown to involve *changes in the dynamics* of the constituent parts of the structure. The Cl,N layer has mainly been studied by means of ¹⁴N and ³⁵Cl NQR spectroscopy,^{14,15} whereas the *n*-alkylammonium chains have been characterized with the help of IR/Raman¹⁶⁻¹⁸ as well as ¹H and ¹³C NMR spectroscopy,^{5,12} An incoherent quasielastic neutron scattering (IQENS)¹⁹ and a ²H NMR²⁰ investigation are also under way.

The polar heads of the *n*-decylammonium chains are anchored, via hydrogen bonds, in a cavity built of chlorine atoms. In phase α the ammonium group occupies with equal probability one of four equivalent sites (orientations) on the time average. This dynamical exchange results in a 4-fold axis in the structure description. During the $\alpha \rightarrow \beta$ transition the chlorine cavities are so distorted that the motion becomes *biased*: the occupation probabilities of two of the sites is increased at the expense of the other two. In the $\beta \rightarrow \delta$ transition (which might proceed in two steps) the cavities are even further warped such that only one favorable site remains in which the NH₃ group is locked. Concomitantly, the b translation period is doubled (due to changes in the chain packing, vide infra). There are twice as many nitrogen positions therefore, all equivalent, however. In the course of the $\delta \rightarrow \epsilon$ transition, finally a stabler hydrogen-bonding network is formed and the two formerly equivalent nitrogen positions become nonequivalent.

The aliphatic chains are believed⁶ to be in a "treelike" state in phase α . (In this state alternate C–C bonds are perpendicular to the Cl,N layers, their torsion angles being T, G⁺, or G⁻ with equal probability, whereas the torsion angles around the horizontal C-C bonds are invariably trans; see Figure 2c.) Unequivocal evidence for this hypothesis is, unfortunately, lacking to date. During the $\alpha \rightarrow \beta$ transition a major rearrangement of the chains takes place: their lateral movements become restricted and they extend from a partially curled state (i.e., conformations containing kinks, G forms, and GTG or GG sequences resulting in somewhat coiled up or contracted chains), thus expanding the basal spacing.⁶ In phase β the area per chain of over 23 Å² indicates a still very loose packing of the chains. This area is further decreased to 22 $Å^2$ in the $\beta \rightarrow \delta$ transition during which two chains formerly equivalent with respect to the b translation differentiate; by so doing, they transform a $\{\sigma_x|000\}$ mirror plane into a $\{\sigma_x|0^1/20\}$ glide plane while doubling the b translation period. The chains finally adopt a more compact packing after the $\delta \rightarrow \epsilon$ transition in which they tilt off the average $\{\sigma_x|0^1/20\}$ glide plane. All the studies conducted so¹³⁻¹⁵ far led to a rather satisfactory

All the studies conducted so¹³⁻¹⁵ far led to a rather satisfactory model for the dynamics of the Cl,N layers in the C10Cl system. Of course, measurements should be extended beyond 90 °C in view of a possible metastable phase observed⁶ between 100 and 120 °C and of the extraordinary changes occurring in phase α between 50 and 130 °C.

The description of the conformational changes in the ndecylammonium chains is much vaguer. Only two findings may be considered *corroborated*:

(i) There exist various conformational defects¹⁶⁻¹⁸ in phases ϵ , β , and α ; their number increases upon raising the temperature.

(ii) The chains can be approximated,²⁵ on the time average, by cylinders of electron density in phases ϵ , δ , and β .

Beyond these facts, a useful Landau-type model has been worked out,⁸ which accurately describes the chain separation during the reconstructive phase transition in terms of an *effective* chain diameter, but, of course, fails to answer the following "microscopic" questions:

(i) Which molecular vibrations are crucial to chain separation?

(ii) What is the distribution of chain conformers in phase α ? (iii) What are the conformations of the chains in phases β , δ ,

and ϵ ? (iv) What causes the pretransition effects (anomalous expansion of the *b* axis and the β angle upon approaching the $i \rightarrow \delta$ transition) in phase i?



Figure 2. Representation of the three structure types expected for C10Cl: (a) phase i; (b) phases β , δ , and ϵ ; (c) phase α (occupancies: a = 1/3, b = 1/9, and d = 1/27).

TABLE I

label	
	n
DaC10Cl	0
D _β C10Cl	1
DyC10Cl	2
DSC10Cl	3
DeC10C1	4
	DγC10Cl DδC10Cl DεC10Cl

(v) Can the oblate shape of the displacement ellipsoids of the carbon atoms and their particular disposition¹⁰ in phase i be rationalized in terms of a vibrational model?

(vi) How can a structure be stable despite a noncompact p cell? (vii) Why does phase α not adopt a pseudohexagonal symmetry (like the C phase of potassium caprate²⁴)?

It was in the hope of elucidating some of the questions above that we undertook the present investigation. In it we shall try to weave existing spectroscopic findings¹³⁻¹⁸ and novel results from vibrational spectroscopy and X-ray diffraction into a more complete picture of the phase transitions in C10Cl.

The labels and abbreviations listed in Table I will be used throughout the text.

Experimental Details

(a) Chemical Syntheses. The tetrahydrofuran (THF) and ether were freshly distilled from sodium/benzophenone under argon. The dimethyl sulfoxide (DMSO), hexamethylphosphoramide (HMPA), acetonitrile, and acetonitrile- d_3 were dried over 4Å molecular sieves. All other reagents were used as received from either Fluka AG or Aldrich Chemical Co. The identities of each intermediate compound were verified by gas chromatographic comparison to authentic undeuterated compounds.

Preparation of n-Decylammonium Chloride (1a) (Scheme 1). n-Decylammonium chloride was prepared by bubbling hydrogen chloride through n-decylamine (Aldrich, purity 99%) (see Chart I).

Synthesis of N,N,N-Trideuteriodecylammonium Chloride (1b) (Scheme I). The ND₁ derivative was prepared by successive exchanges in D₂O; its isotopic enrichment was estimated to be greater than 95% from IR measurements.

Preparation of 1,1-Dideuteriodecylammonium Chloride (2a) (Scheme 2). Decanenitrile (7.65 g) in 20 mL of dry ether was added slowly to a suspension of 2.6 g of lithium aluminum deuteride in 40 mL of ether. After completion of addition, the mixture was refluxed for several hours followed by the workup suggested in Fieser and Fieser.²⁶ The product was then filtered, and the ether was removed by rotatory evaporation. The amine (5.6 g) was then bulb-to-bulb distilled at aspirator pressure. Finally, the amine hydrochloride was prepared as described above.

Preparation of 2,2-Dideuteriodecylammonium Chloride (2b) (Scheme 3). Perdeuterioacetonitrile (2.2 g) was added to 50 mL of THF and 37 mL of 1.3 M n-butyllithium in hexane at -78 °C. After 20 min at this temperature, the white suspension was transferred via cannulae to an addition funnel charged with argon.

This suspension was then added dropwise to a stirred solution of 9.2 mL of bromooctane in 50 mL of THF at -78 °C. After the addition was completed, the solution was allowed to warm to room temperature, and 50 mL of saturated NaCl solution was added. The layers were separated, and the organic phase was dried over MgSO₄. The solvent was removed by rotatory evaporation, and the residue was bulb distilled at aspirator pressure. The separation of the nitrile (3.1 g) from the bromooctane was very difficult but could readily be achieved by preparatory gas chromatography. This nitrile was then reduced with lithium aluminum hydride and treated with HCl by the procedure mentioned above to give 2b.

Preparation of Dideuterioalkyl Bromides (3a, 3b, 3c) (Scheme 4). The appropriate methyl ester (0.16 mol) was dissolved in 25 mL of ether and added dropwise with stirring to $LiAlD_4$ (0.09 mol) in 200 mL of ether. The addition was carried out under N₂. When the addition was completed, the slurry was refluxed for 2

CHART I Scheme 1

Scheme 2

$$CH_3(CH_2)_8CN \xrightarrow{(1)}_{(2)} HCl$$
 2a

Scheme 3

$$\begin{array}{c} CY_{3}CN & \underbrace{(1) \quad n \text{-BuLi/THF} \ (7 = -78 \ ^{\circ}C)}_{(2) \quad CH_{3}(CH_{2})_{6}(CX_{2})Br} & \begin{array}{c} 2b \quad (Y = D, \ X = H) \\ \hline 2c \quad (Y = H, \ X = D) \\ \hline (3) \quad L|A|H_{4} \\ \hline (4) \quad HC| \end{array}$$

Scheme 4

s

$$\begin{array}{c} \mathsf{CH}_{3}(\mathsf{CH}_{2})_{n}\mathsf{CO}_{2}\mathsf{CH}_{3} & \underbrace{(1) \quad \mathsf{LiAID}_{4}}_{(2) \quad \mathsf{PBr}_{3}} \quad \mathsf{CH}_{3}(\mathsf{CH}_{2})_{n}\mathsf{CD}_{2}\mathsf{Br}_{3}\\ & \textbf{3a} \quad (n=6)\\ & \textbf{3b} \quad (n=5)\\ & \textbf{3b} \quad (n=4)\\ \end{array}$$
 Scheme 5
$$\begin{array}{c} \textbf{3b} & \underbrace{(1) \quad \mathsf{Mg}; \ \mathsf{THF}}_{(2) \quad \mathsf{BrCH}_{2}\mathsf{CH}_{2}\mathsf{O}\mathsf{THP}; \ \mathsf{CuCN}; \ \mathsf{THF}/\mathsf{HMPA}} \quad \textbf{2d}\\ & \underbrace{(3) \quad \mathsf{H}^{*}_{aq}}_{(4) \quad \mathsf{PBr}_{3}}\\ & \underbrace{(5) \quad \mathsf{NaCN}; \ \mathsf{DMSO}}_{(6) \quad \mathsf{LiAIH}_{4}}\\ & \underbrace{(7) \quad \mathsf{HCI}}\\ \end{array}$$
 Scheme 6
$$\begin{array}{c} \textbf{3c} & \underbrace{(1) \quad \mathsf{Mg}; \ \mathsf{THF}}_{(2) \quad \mathsf{BrCH}_{2}\mathsf{O}_{3}\mathsf{Br}; \ \mathsf{CuCN}; \ \mathsf{THF}/\mathsf{HMPA}} \quad \textbf{2e}\\ & \underbrace{(3) \quad \mathsf{NaCN}; \ \mathsf{DMSO}}_{(4) \quad \mathsf{LiAIH}_{4}}\\ & \underbrace{(5) \quad \mathsf{NaCI}}_{(5) \quad \mathsf{HCI}}\\ \end{array}$$

h. The reaction was quenched as before. After filtering off the salts, the solution was dried and the ether was removed by rotatory evaporation. The residue was distilled yielding the desired alcohol.

This alcohol was then added to 1.3 M equivalents of PBr₃. When the addition was completed, the orange mixture was kept at 70 °C overnight. After cooling to room temperature, water was added carefully. The organic layer was taken off, and the aqueous layer was then washed with ether. The combined organic layers were dried. The desired deuterated alkyl bromide was separated by distillation from ether.

Preparation of 3,3-Dideuteriodecylammonium Chloride (2c) (Scheme 3). This was prepared by the same procedure as for 2b but using acetonitrile and 1,1-dideuteriobromooctane (3a).

Preparation of 4,4-Dideuteriodecylammonium Chloride (2d) (Scheme 5). The Grignard reagent of 3b was prepared for further reaction in the following manner. 3b (15 g) was added dropwise with stirring to 2.0 g of Mg in 72 mL of THF under N_2 . Bromoethanol (10.4 g) and dihydropyran (7.0 g) were combined slowly. After the exotherm had subsided, 40 mL of THF, 10 mL of HMPA, and 7.4 g of CuCN were added under N_2 . The Grignard reagent was then slowly added via syringe to the stirred suspension. After the mixture had cooled to room temperature, the salts were removed by filtration. The THP ether was then hydrolyzed by stirring with 25 mL of 6 N HCl. Ether was then added to separate the layers. The organic phase was then washed 3 times with saturated NaCl solution, then dried, and the solvent was removed by rotatory evaporation. The crude alcohol was then treated with PBr₃ as described previously to give γ -dideuteriononvlbromide.

This alkyl bromide (2.0 g) was then added to 1.0 g NaCN in 15 mL of DMSO and then heated at 100 °C for 2 h. Water and ether were added and the organic layer was separated. The aqueous layer was washed twice with ether. The organic phases were combined and washed twice with water to remove any DMSO. After drying and solvent removal, the crude γ -dideuteriodecanenitrile was reduced to the amine and treated with HCl, as before, to give 2d.

Preparation of 5,5-Dideuteriodecylammonium Chloride (2e) (Scheme 6). The Grignard reagent of 3c (0.07 mol), prepared as described above, was added to 14 g of 1,3-dibromopropane and 6.3 g of CuCN in 40 mL of THF and 10 mL of HMPA under N₂. After cooling to ambient temperature, ether and water were added, giving rise to two layers from which the organic layer was separated. The water layer was washed twice with ether, and the ether layers were combined. This combined layer was washed several times with saturated NaCl solution to remove any HMPA. Then it was dried, and the solvent was removed. The residue was then treated with NaCN as before. The resulting nitrile was then reduced and the amine was then treated with HCl giving 2e.

(b) X-ray Diffraction. Guinier photographs of C10Cl at various temperatures were recorded on a HUBER high temperature camera 631-632 using copper radiation ($\lambda = 1.540562$ Å). At each temperature the film was exposed for 2 h before the temperature was raised by 1 °C. The lines from the Guinier photographs were indexed with the help of an indexing program.²² The single-crystal experiments are described elsewhere.^{6,10}

(c) Spectroscopic Procedures. Raman powder spectra were recorded on a Coderg T800 spectrometer equipped with a triple monochromator. Sample temperatures were regulated by means of a Coderg CRN2 continuous nitrogen flow cryostat and fluctuated less than 1 °C. The spectral slit widths varied from 1 to 3 cm⁻¹. The 514.5-nm line of a Spectra Physics Ar ion laser Model 171 was used for excitation. The samples endured laser powers up to 250 mW, but for some measurements the beam had to be defocalized.

Infrared spectra were collected on both poly- and monocrystalline samples. Polycrystalline films were prepared on CsI windows; in order to avoid a preferred orientation of the crystallites, the films were deposited by rapid evaporation of ethanolic solutions. The spectra were recorded with a Bruker 113V FTIR interferometer equipped with an MCT detector or a bolometer in the far-infrared region. The samples were in an evacuated sample chamber where temperatures were stable within 1 °C. The resolution was 1 cm⁻¹ and 400 scans were accumulated. The spectra of a monocrystalline platelet were recorded on a Perkin-Elmer 180 spectrometer. The incident electric field was parallel to either the a or the b axis. As the crystals are destroyed during the i $\rightarrow \delta$ transition, polarization measurements were made in phase i only.

Structural Analysis

The various phases of C10Cl and their interconnecting transitions are represented in Figure 1 together with some of their characteristics. The manner in which these data were obtained is detailed elsewhere.⁶ Suffice it to say that cell constants of phases α, β, δ , and ϵ were found by indexing powder diagrams, while the lattice parameters of phase i were determined in a single-crystal diffraction experiment.¹⁰ The different structures which C10Cl may adopt are depicted in Figure 2.

Phase i represents the ground state (Figure 2a) of the C10Cl system. It crystallizes¹⁰ spontaneously at room temperature under almost all conditions and is stable between -195 and 39 °C. In a sample heated past this latter temperature, a reconstructive phase transition to phase δ occurs during which chain separation takes place^{6,8} (Figures 1 and 2). After two more degrees phase δ merges into phase β via another transition, this one of order-disorder or displacive type. At 43 °C finally, phase α is reached by way of a reconstructive phase transformation.

Upon *cooling*, the $\alpha \rightarrow \beta$ and $\beta \rightarrow \delta$ transitions occur in reverse order. At 39 °C, however, the $\delta \rightarrow i$ transition does not take place. Instead, at 29 °C, a new phase, ϵ , appears, still of the noninterdigitated type. Phase ϵ is *metastable*, for, at room temperature, it is transformed back into phase i after a few weeks. Another feature of the $\epsilon \rightarrow i$ transition, worth mentioning, is its being susceptible to pressure.

Phase α (Figure 2c) is "isomorphous" to phase α [C6]. This crystallizes as conglomerate⁶ of tiny, intergrown platelets with respect to (001) and adopts the tetragonal system. The chlorine atoms constitute quite a rigid square lattice, whereas the cations are necessarily disordered. Each chlorine with its four nearest chlorine neighbors forms a square pyramidal cavity in which the polar head fits. Of the chains, only their projections onto the caxis could be determined. This can be rationalized in terms of a "tree model" (Figure 2c) in which every other C-C bond is perpendicular to the Cl,N layers and the corresponding torsion angle is disordered between G⁺, G⁻, and T.²⁴ The layer of hydrocarbon chains is very loosely packed, as witnessed by the unusually spacious area per chain of 25 $Å^2$.

Phase β is stable within 2 °C only. Because of this narrow temperature range Guinier photographs usually contain lines from the adjacent phases as well and their interpretation is formidable and ambiguous. Nevertheless, we speculate that the a and/or blattice parameters are intermediate between the ones of phases α and δ . The slight decrease of the c axis during the $\delta \rightarrow \beta$ transition, on the other hand, is quite certain.

Phases δ and ϵ are "isomorphous" to phase δ [C8]. At ambient temperature, this latter²⁵ grows in delicate, curved chips. It is monoclinic and, based on its unit cell, phases δ and ϵ could be indexed in the orthorhombic and triclinic systems, respectively. In phase δ [C8] a linear hydrogen-bonding scheme is formed: infinite chains along the a axis. The chains adopt an all-trans conformation on the average and subtend an angle of 75° with the b axis. This tilt results in an area per chain of 22 Å². The p cell (a = 4.7 Å, b = 8.8 Å; c = 2.5 Å, space group Ammm) is reminiscent of the p cell M_{\parallel} or, possibly, $T_{\parallel}^{27,28}$ By comparing the area per chain in the p cell of δ [C8] with the one typically found in compact layer structures, it becomes evident that the hydrocarbon chains are not very tightly packed in phase δ [C8].

There are two major differences between phases δ and ϵ : in phase ϵ , the chains are packed less loosely and the hydrogenbonding network is slightly distorted with respect to phase δ .

Vibrational Analysis

If the correlation times governing the dynamics of the ndecylammonium ions in the disordered phases are long enough $(\tau_c \gg \text{picoseconds})$, vibrational spectroscopy enables us to observe all positions and conformations of the hydrocarbon chains. Furthermore, by selectively deuterating the carbon atoms, it is possible to map out the chain conformation site by site, since the CD₂ rocking mode frequency depends on the local conformation.²⁹⁻³³ Finally, by deuterating the ammonium group, the changes in its environment can be detected.

As to the *notation*, we shall use ν , δ , and r to label the stretching vibration and the bending and rocking deformations, respectively.

I. Study of the Interdigitated Phase (Phase i). The factor group of this phase is isomorphic to the point group 2 (C_2). A chain consists of 35 atoms. As the symmetry of each molecule is 1 (C_1), each of the 99 internal vibrations gives rise to a component in each symmetry species of the factor group. Each mode is infrared and Raman active.

According to X-ray results, the n-decylammonium chains are in the all-trans conformation. Their spectra may therefore be analyzed like those of solid *n*-alkanes or extended *n*-alkylammonium chains in perovskites. To confirm our interpretation, we applied a normal-coordinate treatment to the all-trans chains, using a standard tetrahedral geometry [i.e., bond lengths d(C-C)

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Figure 3. Infrared spectra between 1120 and 1650 cm⁻¹: (a) phase i at 293 K; (b) phase δ at 310 K; (c) phase α at 338 K; (d) phase α at 363 K; (e) phase ϵ at 293 K; (f) phase ϵ at 80 K.

TABLE II

	phase i	freq, cm ⁻¹	phase ϵ	freq, cm ⁻¹	
DC10Cl	IR	230	IR	209, 226	
	Raman	216, 228	Raman	212, 226	
C10Br	Raman	218, 229	Raman		
CIICI	Raman		Raman	205	
C12Cl	Raman	183			
C13Cl	Raman	167			
C14Cl	Raman	160			

= 1.543 Å, d(C-H) = 1.093 Å, d(N-C) = 1.48 Å, d(N-H) = 0.97 Å and bond angles of 109.47°]. The force field obtained for the n-alkylammonium ion in perovskites was used.³⁴

A number of vibrations correspond to nonlocalized modes and are sensitive to both length and configuration of the chains. They give rise to progression bands which are mainly observed in the infrared spectrum (Figure 3). The Raman frequency of the longitudinal acoustical mode, LAM-1, is 216 cm⁻¹ (Figure 4); it is slightly higher than in the corresponding³⁵ *n*-alkane, 209 cm⁻¹, as expected for a chain engaged in hydrogen bonds (Table II). A weak shoulder is observed at higher frequency; this diffusion has been assigned to the transverse acoustical mode, TAM-4, in solid *n*-undecane.³⁶ Two intense absorptions (Figure 4b) at 234 and 210 cm⁻¹ probably contain a participation of the hydrogen bonds, and the LAM-1 appears as a shoulder. At 80 K, this system of three bands appears in both the infrared and the Raman spectra. Intensities and the relatively important shift of the highest frequency suggest a coupling of the hydrogen bond with the TAM-4.

In the Raman spectra of DC10Cl and C10Br and the infrared spectrum of DC10Cl, only two bands, corresponding to LAM-1 and TAM-4, are found. In other CnCl compounds, crystallized in phase i, the LAM-1 is observed as a single line in the Raman spectrum, at a frequency slightly higher than that of the corresponding *n*-alkane, when n < 12, or, at about the same value, when $n \ge 12$. In all these compounds, the hydrogen-bond frequency does not coincide with that of a skeleton deformation, and the corresponding band is not observed, due to its weak intrinsic intensity in Raman scattering.

In the Raman spectrum, the most intense bands (Figure 5) corresponds to the limit modes $\varphi_k = 0$ and $\varphi_k = \pi$ of an infinite *n*-alkyl chain (φ_k is the phase difference between the movements of adjacent oscillators). Some of these bands contain a noticeable participation of NH₃ group motion; they are shifted or disappear after deuteration of the ammonium group. For example, the lines at 1162 and 1117 cm⁻¹ are replaced by one intense absorption at 1130 cm⁻¹ and those at 1056 and 946 cm⁻¹ become less intense.



Figure 4. Spectral domain between 150 and 300 cm⁻¹: (a) Raman spectra; (b) infrared spectra.



Figure 5. Raman spectra of C10Cl between 825 and 1200 cm⁻¹. The top and bottom spectra are from DC10Cl.

The corresponding modes involve NH₃ rocking.

Localized modes correspond to vibrations of a limited part of the chains; their frequency depends on the local conformation only and is independent of the chain length. The r(CH₃) frequency at 886 cm⁻¹ in the Raman spectrum, e.g., corresponds to a trans conformation in the vicinity of the methyl group. The $r(ND_3)$ transition is observed at 818 cm⁻¹. In the infrared spectra, the $\delta_s(NH_3)$ at 1370 cm⁻¹, and the $\delta_s(NH_3)$ and $\delta_a(NH_3)$ near 1520 cm^{-1} and 1600 cm^{-1} , respectively, are other examples of localized vibrations (Figure 3). The $r(CD_2)$ frequencies depend on the local conformations, too. D β C10Cl, D δ C10Cl, and DeC10Cl were obtained in phase i (Figure 6). For the latter two, the $r(CD_2)$ frequency is 622 cm⁻¹, which is the value characteristic of trans conformations on both sides of the CD₂ group;³⁴ the $r(CD_2)$ frequency for D β C10Cl, corresponding to the same sequence TT, is slightly higher, 630 cm⁻¹, due to the proximity of

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Figure 6. Infrared spectra of the selectively bideuterated derivatives. (The numbers by the spectra indicate the temperatures [°C] at which they were recorded.) (a) $D\alpha C10Cl$; (b) $D\beta C10Cl$; (c) $D\gamma C10Cl$; (d) $D\delta C10Cl$; (e) $D\epsilon C10Cl$.



Figure 7. Raman spectra of the C-H stretching domain.

the ammonium group.³⁴ A weak absorption near 660 cm⁻¹ stems probably from a CHD impurity vibration.²⁹ In the spectrum of D ϵ C10Cl a weak feature near 669 cm⁻¹ is due to an imperfect compensation of sample and reference spectra.

In conclusion, the study of both the nonlocalized and localized modes confirms the *trans* and *planar* structure of the *n*-decyl-ammonium chains as determined by X-ray diffraction.

In the Raman spectrum, the domain of the CH stretching modes (Figure 7) presents well defined maxima. The $\nu_a(CH_2)$ frequency, 2883 cm⁻¹, has the value of the corresponding *n*-alkane; this coincidence is consistent with the existence of long trans segments in the chains.³⁸ The peaks at 2870, 2930, and 2961 cm⁻¹ belong to the methyl stretching vibrations; the other ones and the broad signal between 2850 and 3000 cm⁻¹ are characteristic of extended methylene chains and due to Fermi resonance between the $\nu_s(CH_2)$ and the quasi-continuum of the bending progression band overtones.³⁷ A splitting (Figure 8) due to the crystalline field is observed for the $\delta(CH_2)$ frequency. The most symmetrical component is at 1419 cm⁻¹; this value is very close to the one in



Figure 8. Raman spectra of the C-H bending domain.

polymethylene and indicates strong interactions in the unit cell. The other component, at 1442 cm⁻¹, is flanked by several maxima at higher frequency: their intensity is due to Fermi resonance with overtones and combinations of $r(CH_2)$ transitions.^{39,40}

The spectra are typical of an ordered solid; the low-frequency Raman spectrum consists of narrow lines. Furthermore, some vibrations are split into two components due to intermolecular coupling, e.g., the absorptions at 1370 and 1515 cm⁻¹, assigned to $\delta_{\rm s}(\rm CH_3)$ and $\delta_{\rm s}(\rm NH_3)$, respectively, and the $r(\rm CH_2)$ fundamental at 720 cm⁻¹.

The $\nu(NH_3)$ modes cannot be studied since they appear as ill-defined absorptions on the high-frequency side of the C-H stretching domain. The infrared spectrum of DC10Cl (Figure 9) presents three maxima in the N-D stretching range: at 2145, 2226, and 2264 cm⁻¹. These develop into seven bands that are difficult to assign at 95 K. In the spectrum of an isotopic dilution (about 10% of DC10Cl), a band appears at 2175 cm⁻¹, and that

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⁽³⁸⁾ Ricard, L.; Abbate, S.; Zerbi, G. J. Phys. Chem. 1985, 89, 4793. (40) Abbate, S.; Zerbi, G.; Wu

⁽⁴⁰⁾ Abbate, S.; Zerbi, G.; Wunder, S. L. J. Phys. Chem. 1982, 86, 3140.



Figure 9. Infrared spectra of the ND₃-stretching vibrations: (a) phase i; (b) phase ϵ . (1, 2) DC10Cl in C10Cl (~10%); (3, 4) DC10Cl.

at 2145 cm⁻¹ vanishes: they can be assigned to combinations of two fundamental vibrations of C10Cl and DC10Cl, respectively. The peak at about 2265 cm⁻¹ which exists in the spectra of both C10Cl and DC10Cl is probably also due to a combination. The absorption at 2226 cm⁻¹ is split into three peaks at 2229, 2216, and 2196 cm⁻¹ which must correspond to three different ND bonds. Assuming an isotopic ratio of 1.35, this assignment leads to NH₃ frequencies between 2960 and 3010 cm⁻¹; these values are quite consistent with the infrared spectrum of C10Cl. At 95 K, at least five bands are found in this domain. Since the NH₃ groups are in general positions in a unit cell containing two molecules, six stretching modes, active in infrared and Raman, are expected: this number can explain the observed features.

The asymmetric NH_3 deformation mode (Figure 3a) is split into four components: two peaks and two shoulders. Polarization measurements show that the highest two transitions belong to the B symmetry species of the factor group and the other two to the species A. There are two fundamental vibrations which can be assigned to N-H engaged in different hydrogen bonds in agreement with the discussion in the preceding section.

Thus, this study gives evidence for the existence of *inter*- and *intramolecular coupling* in trans planar chains and the *none-quivalence of the three N-H bonds*. At about 80 K, the spectra show a slight improvement of the resolution but are not modified otherwise. This behavior indicates a weak mobility of the chains due to a very dense packing.

II. Study of the Noninterdigitated Phases. (a) Phase δ . Changes in the spectra between phase i and phase δ are important; they are of three types:

1. Features characteristic of fully extended chains are lost and new bands appear.

2. The frequencies and intensities of the transitions involving the ammonium group are modified.

3. Intermolecular interactions become weaker.

1. The intensity of the progression bands decreases and their width increases; this is observed in both infrared and Raman spectra. The intense peak of the LAM-1 is replaced with a wider band (Figure 4a) of which the maximum is at 225 cm⁻¹. This indicates the presence of *several not-entirely extended conformers*.

In the CH bending domain (Figure 8), the intensity of the band at 1465 cm⁻¹, assigned to the intramolecular coupling of trans forms, strongly diminishes with respect to the methyl vibrations at 1455 cm⁻¹. The $v_a(CH_2)$ peak (Figure 7) is less intense and the frequency of the $v_s(CH_2)$ line shifts upwards by about 2 cm⁻¹ as the size of the trans sequences decreases.³⁸ The peak intensity

T	A	BL	Æ	III	

	phase δ, %	phase ϵ , %	
TTTTT	42	72	
TTTGT	23	13	
TGTTT	23	13	
TGTGT	12	2 (TGTG'T)	

near 2940 cm⁻¹ increases with regard to that of the 2850-cm⁻¹ line. These features and the presence of a diffusion band at 1077 cm⁻¹ reveal the occurrence of *gauche bonds*.

The type of defects can be specified by means of an analysis of the spectra and packing considerations. Within the accuracy of our measurements we were unable to detect GG sequences (there is no absorption near 1355 cm⁻¹ in the infrared spectrum). But there is a Raman signal at 875 cm⁻¹ and an infrared band at 1340 cm⁻¹ (Figure 3) which are characteristic of gauche forms in the vicinity of the methyl end, and a wide infrared band at 1307 cm⁻¹ arising from GTG or GTG' sequences;³⁴ the other band associated with these structures, near 1367 cm⁻¹, is hardly visible as a shoulder of the absorption at 1378 cm⁻¹. A spectroscopic study of the phase δ [C8] shows the same types of defects.²⁵ Since phases δ [C10] and δ [C8] are isomorphous and since, in C8C1, the chains are approximately parallel and not too loosely packed,²⁵ defects of the GTG type are excluded.

But the gauche linkages can be more accurately localized with the help of the selectively deuterated derivatives (Figure 6). The spectrum of D α C10Cl shows only one absorption at 662 cm⁻¹ due to a trans conformation around the C₁-C₂ bond.³⁴ In the spectra of the other bideuterated derivatives, two $r(CD_2)$ bands are observed: D β C10Cl (656 and 632 cm⁻¹); D γ C10Cl (651 and 626 cm⁻¹); D δ C10Cl and D ϵ C10Cl (651 and 622 cm⁻¹). A frequency of ~650 cm⁻¹ indicates the existence of one G form around one of the C-C bonds adjacent to the carbon atom under study (TG or GT sequence); a value of ~620 cm⁻¹ is characteristic of a TT sequence.

The intrinsic intensities of the vibrations assigned to TG and TT structures have been shown to be nearly equal for the δ -bideuterated *n*-decylammonium ion;³⁴ thus the integrated intensities of the bands are a direct measure of the relative population of each conformation. But the proximity of the NH₃ group modifies the $r(CD_2)$ frequencies in the β -bideuterated derivative, and nothing is known about the intrinsic intensities. An estimation of the TT concentration in each phase can be obtained by measuring the modification of the integrated intensity of the corresponding band with respect to the total intensity of the $r(CD_2)$ absorption domain. One finds approximately 60% of TT structures in phases δ and α . An evaluation of the relative population of each structure under the assumption of nearly equal intrinsic intensities of the bands leads to the same result. These measurements were performed on a sample which did not present the CHD impurity band. We thus believe that the hypothesis of nearly equal intrinsic intensities for the $r(CD_2)$ vibrations due to TG and TT conformations in D β C10Cl and D γ C10Cl is a satisfying approximation, and we used it in order to evaluate the relative concentrations of the two types of structures in the different phases. For D δ C10Cl and D ϵ C10Cl, the proportion of TT and TG(GT) conformations were obtained from the evaluation of the TT band intensity weakening. In phase δ one finds a comparable population of GT structures around carbon atoms 2, 3, 4, and 5, between 32 and 38%. Since all $N-C_1-C_2-C_3$ segments are trans, these percentages imply that about 35% of the C_2-C_3 and C_4-C_5 bonds have a gauche conformation and almost all the C_3-C_4 and C_5-C_6 bonds are trans. The conformers present are shown in Table III.

All available data obtained from other techniques indicate the presence of a $\{\sigma_x|0^1/20\}$ glide plane; there are four molecules in a unit cell and the maximal multiplicity is four.²⁵ Our spectroscopic results are not compatible with this structure unless one assumes an interconversion between the different types of conformers through kink (GTG') diffusion along the chains.

2. The most important modifications in frequency and intensity affect the bands containing a participation of the NH_3 vibrations. Examples in the Raman spectrum are the lines at 1162 and 946

 cm^{-1} (shifted to 1148 and 926 cm^{-1}) and the absorption at 1056 cm⁻¹ (reduced intensity). The asymmetric NH₃ deformation bands collapse to a broad hump of which the maximum is shifted to a lower frequency. This behavior indicates a radical rearrangement of the NH_3 environment.

3. The $\delta_s(CH_3)$ frequency increases from 1370 to 1378 cm⁻¹. This increase is typical of a strong diminution of the interactions between the chain layers in *n*-alkanes.^{31,41} Splittings due to the crystalline field disappear; intermolecular interactions are therefore weaker in this phase.

It is interesting to note that the factor group splitting starts vanishing gradually already within phase i when the temperature approaches 42 °C, i.e., the i $\rightarrow \delta$ transition. Bands characteristic of conformational defects, on the other hand, begin to appear upon approaching this transition.

In conclusion, the conformational disorder of the hydrocarbon chains is important in phase δ ; it involves kink (GTG') defects which allow the chain axes to remain parallel as is indicated by X-ray measurements. The methyl ends become more flexible. Intermolecular interactions are weak. Finally, the linkage of the NH₃ heads to the N-Cl cavity is radically different from the one in phase i.

(b) Phase α . The analysis of the infrared and Raman spectra reveals an increased conformational disorder with respect to phase δ

1. In the Raman spectrum at 80 °C, the broad DLAM band has a maximum at about 232 cm⁻¹. Chain melting (i.e., the number of different conformers) is more prominent in phase α than in phase δ . The limiting k = 0 mode bands, observed between 1050 and 1120 cm⁻¹, broaden for this reason. Their intensity decreases with respect to the line at 1076 cm⁻¹ characteristic of gauche structures.

The decrease of the intensity of the band at 1463 cm⁻¹ provides further evidence of gauche conformations. The C-H stretching domain shows fundamental changes: the peak intensity of the 2885-cm⁻¹ line collapses and the band melts into the background; the frequency of the $\nu_s(CH_2)$ vibration near 2850 cm⁻¹ increases by 3 cm⁻¹ as the size of the trans sequences diminishes;³⁸ finally, the peak intensity near 2940 cm⁻¹ increases with regard to that of the 2850-cm⁻¹ line. All these changes are typical of an increase of the G-form concentration.

2. In the infrared spectrum, the progression bands due to nonlocalized methylene or skeletal deformations broaden and flatten; the intensities of bands increase that are assigned to specific bond sequences and end gauche structures (near 1340 cm⁻¹) and conformational GTG or GTG' sequences, (near 1310 cm⁻¹); moreover, the 1310-cm⁻¹ absorption displays a low-frequency wing which has been related to the presence of kinks at different positions in the chain, in the case of n-alkanes.⁴² This effect strongly increases with temperature.

3. The spectrum of $D\alpha C10Cl$ shows that the C_1-C_2 bond is always trans. The slight shift of the $r(CD_2)$ band toward lower frequencies probably implies noticeable geometrical changes around the NH₃ end. The study of D β C10Cl, D γ C10Cl, D δ C10Cl, and D ϵ C10Cl at 65 °C indicates that about 40% of C_2 - C_3 and C_4 - C_5 are gauche and almost all the C_3 - C_4 and C_5 - C_6 bonds are trans. These proportions do not vary in any noticeable way when the temperature is raised to 105 °C; but the total number of G forms increases (cf., the strong enhancement of defect bands in the IR spectrum of C10Cl at 90 °C). This suggests that the increase in conformational disorder, at the $\delta \rightarrow \alpha$ transition as well as within the α phase, with rising temperature, mainly concerns the part of the chains beyond carbon C_6 .

4. The intensities of the Raman lines involving motion of the NH₃ group decrease, but their frequencies are not modified. This behavior is in concordance with X-ray results which establish that the nitrogen and chlorine atoms lie on almost the same positions in phases α and δ .⁶

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The previous results are compatible with the "treelike" structure proposed from X-ray data of phase α [C6],⁶ if one assumes that the weight of the G and G' conformations is smaller than that of the trans one. In this hypothesis, the C_2 - C_3 and C_4 - C_5 bonds would be perpendicular to the inorganic layers. The number of gauche forms in the first part of the chains is thus only a little higher than in phase δ but the packing is different; it allows GTG sequences which induce quite a different type of chain conformation. The frequency and width of the DLAM band indicates a great variety of conformers and a low percentage of fully extended chains.

(c) Phase ϵ . 1. At 18 °C, the Raman spectrum between 1000 and 1200 cm⁻¹ is characterized by the intense and narrow peaks due to extended chains. The band near 1080 cm⁻¹ caused by gauche forms is very weak. A LAM-1 or DLAM band is observed near 223 cm⁻¹.

The infrared spectrum clearly shows progression bands due to nonlocalized modes of coupled vibrators. Some weak characteristic absorptions of kinks are still observed; the presence of end G forms is hardly detectable. The analysis of the bideuterated derivatives reveals the C_1 - C_2 and C_3 - C_4 bonds to be trans; about 15% of the C_2 - C_3 and C_4 - C_5 bonds are gauche. These results suggest that the chains are mainly in a T_8 conformation, although some specific defects still persist. No factor group splitting is observed, except a weak shoulder at the $\delta(CH_2)$ diffusion band near 1425 cm⁻¹. In the Raman spectrum, the $\nu(CH_2)$ and $\delta(CH_2)$ spectral domains are far less resolved than those of phase i at the same temperature. All these features indicate that intermolecular interactions are weaker in phase ϵ than in phase i. Transitions containing a participation of NH₃ motions give rise to narrow and intense lines, as in phase i, but their frequencies are the same as in phases α and δ . The $r(ND_3)$ frequency of 774 cm⁻¹ is different from the one in phase i.

The N-D stretching domain of an isotopically diluted solution (Figure 9) presents four maxima at both, ambient temperature and 95 K. The bands at 2270 and 2202 cm⁻¹ are far more intense than the absorptions at corresponding frequencies in the spectrum of DC10Cl; thus they can be assigned to two phonon modes of C10Cl. The maxima at 2175 and 2233 cm⁻¹ are less intense than the corresponding ones in DC10Cl and must be assigned to N-D elongations in both cases: 2175 cm⁻¹ to $\nu_s(ND_3)$ and 2233 cm⁻¹ to $\nu_a(ND_3)$. If one applies the isotopic ratio determined⁴⁴ for CH₃NH₃Cl [1.37 for ν_s (ND₃); 1.35 for ν_a (ND₃)], one finds 2980 and 3010 cm⁻¹ for $\nu_s(NH_3)$ and $\nu_a(NH_3)$, respectively, in nice agreement with the observed spectrum. The vibrations of the ND_3 group can thus be interpreted in terms of group vibrations, which means that the N-D vibrators are nearly equivalent.

2. Upon lowering the temperature to about -180 °C, the spectra are modified. Absorptions due to specific chain conformations and the weak Raman band at 1080 cm⁻¹ are no longer observed. In the C-H stretching region, the $\nu_a(CH_2)$ band is very intense and maxima due to intramolecular coupling with the harmonics of the $\delta_s(CH_2)$ progression bands show up on its high-frequency side. The LAM-1 (Figure 4) band is found at 218 cm⁻¹; this is precisely the frequency expected for a fully extended chain. However, the strength and consequently the frequency of the hydrogen-bond elongation are different. This difference manifests in the spectra: coupling with TAM-4 is weaker and, in DC10Cl, the spectrum suggests that $\nu(ND - Cl)$ couples with the LAM-1. In the infrared spectrum, numerous bands are split into two components; in the Raman spectrum, the 1419-cm⁻¹ component of the $\delta(CH_2)$ factor group splitting is observed.

Phase ϵ at low temperatures is thus an ordered crystal with chains in the all-trans conformation and strong intermolecular interactions. The modifications of the spectra upon raising the temperature suggest an increase of the chain mobility and reveal some conformational disorder. As a Guinier-Lenné diagram⁴⁵

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does not indicate any conspicuous structural modifications in the same temperature range, this result implies a loose packing and is consistent with the noninterdigitated structure proposed for phase ϵ from X-ray diffraction measurements. Indeed, such a structure provides a lot of space to neighboring chains and admits some G forms (as kink defects) and easy motions leading to a weakening of the interactions. A small hump in the heat capacity thermogram,⁴⁵ at 214 K, probably corresponds to the onset of these movements through thermal activation.

In phase ϵ , there are two independent chains per asymmetric unit.^{14,25} The spectroscopic results do not show two types of molecular conformations, as was the case in the low-temperature phase⁴³ of $(C_{10}H_{21}NH_3)_2CdCl_4$. The loss of the $\{\sigma_x|0^1/_2 0\}$ glide plane during the $\delta \rightarrow \epsilon$ transition should be rather explained with the help of the chains' tilting off the glide plane and finding a denser packing.

Phase ϵ is essentially different from phase i with regard to the NH₃ environment and the space between the chains. This suggests that the spontaneous transition from phase ϵ to phase i, which takes weeks, principally consists in a modification of the binding of the polar heads to the chlorine matrix, allowing a denser packing.

Conclusions

The combined efforts of vibrational spectroscopy and X-ray diffraction result in a consistent picture of the various structures of C10Cl.

Phase i. This is a well-ordered, 3-periodic structure.¹⁰ All the *n*-decylammonium ions are *entirely* extended. The chains are *interdigitated* and pack according to the p cell O_b^{27} or $O_{\perp}'.^{28}$ Their packing is quite *dense*; it leaves *little* mobility and witnesses a *strong* intermolecular coupling. Chlorine and nitrogen atoms form a two-dimensional, endless hydrogen-bonding network. The N-H···Cl bonds are *not* equivalent and the ammonium groups are locked *rigidly* in *one* position.

Phase δ . This structure is characterized by a considerable dynamical disorder. The aliphatic chains are not interdigitated in this phase; they subtend an angle of ~75° with the b axis. All the chains are not fully extended; they rather adopt several conformations comprising G forms and GTG' kinks. These kinks leave the chains all parallel to one direction. Intermolecular coupling is much weaker than in phase i. This is due to a $\{\sigma_{\mathbf{x}}|0^{-1}/_{2}0\}$ glide plane that is formed on the time average by the diffusion of defects along the chain axes. The N-H···Cl bonding network is fundamentally different from the one in phase i: there are endless chains of hydrogen bonds along the a axis.

Phase α . The disorder (i.e., the number of defects and conformers) in this phase is even greater than in phase δ and strongly increases with the temperature. Torsion angles around the C-C bonds perpendicular to the Cl,N layers are disordered between G⁺, G⁻, and T, whereas the ones around the remaining C-C bonds are T on the picosecond time scale. This distribution of torsion angles leads to treelike chains (Figure 2c) which, when rotating around the vertical C-C bonds, are reminiscent of the *motion of a crankshaft*. The NH₃ environment is quite similar to the one in phase δ ; the ammonium groups are dynamically disordered between four orientations, however. No hydrogen-bond network is realized in phase α .

Phase ϵ . This phase is particular in that considerable changes between ambient and liquid nitrogen temperatures take place and do not manifest in Guinier diagrams. The chains are not interdigitated and may be approximated as T₈ chains. This picture is, however, only true on the time average and in reality there exist a few G forms and kinks at ambient temperature. They disappear, however, gradually upon cooling to ~90 K. At this temperature, there are no defects left and all the chains are in a fully extended state. They probably pack in the M₁₁ or T₁₁ p cell.²⁸ (An orthorhombic p cell cannot be excluded based on spectroscopic evidence, but seems much less likely in view of the structure of phase β .) Despite the strong intermolecular coupling the packing is different and probably *less* compact than in phase i.

Based on the structures presented above, we now propose the following mechanisms for the phase transitions:

 $i \rightarrow \delta$. Upon raising the temperature, the angular fluctuations of the chains and certain molecular *defects* (end G forms and kinks) become excited such that the chains become "thicker and thicker". At the critical temperature this lateral expansion needs that much more space that a *new* structure becomes *more stable*; i.e., the chains separate. Because of this separation the ammonium groups can move closer together and form a new hydrogen-bonding network.

 $\delta \rightarrow \alpha$. During this transition more G forms are introduced into the chains. These partially curl up and, consequently, the *layer spacing* becomes *smaller*. The chlorine cavities acquire the archetypical symmetry while expanding slightly. In this new structure, *GTG defects* are also possible and the interchain coupling becomes minimal.

In conclusion let us try to answer the questions we asked at the onset of this investigation.

(*i* and *iv*) From our analysis it is impossible to put the finger on one particular vibration and say: This triggers the $i \rightarrow \delta$ transition and this is responsible for the pretransition effects. The only manifestation of any pretransition phenomenon within phase i consists in the appearance of G forms near the methyl ends and of GTG' kinks. The creation of these defects along with the loss of intermolecular coupling certainly does not contradict the observed increase in the b and β lattice parameters.

(*ii and iii*) Our study enables us to ascribe specific chain conformations and their interconversion mechanisms to phases ϵ , δ , and α . In phase ϵ the population of the T₈ conformation reaches 100% at liquid nitrogen temperature. Because of the lack of bideuterated derivatives for carbon atoms ζ , η , ω , we cannot specify percentages for all possible conformers.

(*ii*) Clearly our results from the bideuterated derivatives do not contradict the tree model for phase α ; however, they do not actively corroborate it either. The close resemblance of the populations of the conformers in phases α and δ is surprising, considering the obvious differences of the corresponding structures (Figure 2b and c). But since the carbon atoms are subject to different types of motions in the two phases (two-site jumps in phase δ , three or higher site jumps in phase α^{20}), we may confidently accept this accidental similarity.

(v) By summing over all the modes observed in the IR and Raman spectra, one can obtain a displacement tensor that could be compared with the one resulting from the refinement. This computation did not seem worth the effort before it was ascertained that the phenomenon of the particular disposition¹⁰ is not due to an artifact connected to crystal twinning or imperfect absorption correction. Such a study is, unfortunately, left to a hardy successor to our work.

(vi) A word concerning the p cell cited in an earlier section and the picture of an all-trans chain refined for phase $\delta[C8]$ seems in order. For in the p cell Ammm there is certainly too much space available per chain for guaranteeing a stable structure. But the more detailed study of the LAM-1 reveals us that the picture of the T₈ chain is a rather crude approximation for the many different conformers. Since the section of these conformers is larger (e.g., \sim 6 × 6 Å² for a GTG' kink) than that of a T₈ chain, and since the defects diffuse up and down the chain (the dynamical nature is evidenced by numerous NMR studies^{5,8,12}), it appears more realistic to imagine the chains as occupying the volume of an enlarged T_8 chain. The structure is given additional stability by the entanglement of the chains by means of the kinks and other defects. Because of the near-square section of the kinks and their mobility, the occupied volume can be approximated as a cylinder. The volume is obstructed much in the same way as a rotating plane propeller appears as a cycle to our eyes and acts as an impenetrable disk toward any object thrown against it. We learn from this result that the picture of an effective chain diameter⁸ is indeed insightful. The p cell, seemingly unreasonable for all-trans chains, becomes in this light the logical packing for cylinders of electron density.

⁽⁴⁵⁾ We heartily thank Dr. N. B. Chanh and J. R Housty of the Université de Bordeaux, Laboratoire de cristallographie et physique cristalline for these measurements.

(vii) One might expect the chains in phase α to adopt a pseudotrigonal symmetry; they would then resemble cones of electron density. Given the weakness of hydrogen bonding, one might wonder why these cones should not arrange in a hexagonal closest packing (as in the C phase of potassium caprate²⁴). The answer seems to be linked to the existence of chains in a rather extended conformation. Due to them, the chains probably do not adopt a pseudotrigonal symmetry and for this reason do not diffuse past one another too easily.

It is our belief that we have reached a satisfactory level of understanding as to the structures of the phases of C10Cl and their interconversions. Furthermore, we are completing the study of the bideuterated derivatives and of the structure of phase δ [C8] stable below 0 °C. This knowledge will advance our understanding of the C10Cl system to a point of purring satisfaction. There remain to be studied the time regimes of the various molecular motions for completing the picture; these investigations^{19,20} are under way and will be presented in future publications. Incoherent QENS is expected to provide information on motion in the 100-1000-ps time domain and ²D NMR will help identify the nature of the motion in the various phases.

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Vibrational Assignment, Normal-Coordinate Analysis, and Vibrational Optical Activity of **Chlorofluoroacetic Acid and Chlorofluoroacetate**

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In the first part of this paper, we report detailed vibrational spectra and an empirical normal-coordinate analysis of one of the simplest chiral molecules, chlorofluoroacetic acid, as well as its anion, chlorofluoroacetate. To allow for an unambiguous vibrational assignment, deuterium isotopomers were prepared and studied as well. In the second part, vibrational optical activity data are reported and discussed.

Introduction

Vibrational optical activity (VOA) was experimentally verified in both absorption and light scattering in the early 1970s.¹ The two VOA experiments, infrared vibrational circular dichroism (VCD)² and Raman optical activity (ROA),³ offer the possibility to sample molecular dissymmetry or asymmetry via vibrational transitions, unlike classical circular dichroism, which samples the molecular chirality via electronic transitions. The large number of accessible vibrational transitions, and their established sensitivity to molecular structure, had made VOA a long anticipated technique in molecular spectroscopy. Indeed, an enormous amount of spectroscopic knowledge of chiral species has been acquired over the past decade: VOA spectra reveal novel information on the details of molecular vibrational states, origins of vibrational intensity and, of course, molecular conformation and structure.¹

The interpretation of VOA spectra, however, is still in its infancy. One of the earliest models for the interpretation and computation of both VCD and ROA intensities is the coupled oscillator mechanism,⁴⁻⁶ which was transferred from the theory of electronic circular dichroism. Aside from some other models with limited applicability, little empirical information has been collected which would allow the prediction of strong and weak features in VOA. In addition, the lack of, or the low degree of, symmetry in the molecules makes the vibrational assignment very tedious and often somewhat ambiguous. Up to very recently, empirical force fields have been used to obtain the atomic displacement vectors necessary for any computation of VOA intensities. Such empirical force fields on chiral molecules are always indeterminate to some degree, and depend on the availability of isotopic data. Recently,7 some promising progress has been made in the ab initio computation of molecular force fields as well as vibrational and VOA intensities.

In this publication, we report the vibrational spectra and an empirical force field (Urey-Bradley) of chlorofluoroacetic acid and chlorofluoroacetate. These species were selected since they are among the smallest, noncyclic chiral molecules which can be resolved into the enantiomers via diastereomeric crystallization. Furthermore, collection of the VOA data is greatly simplified by the fact that the acid is a clear, colorless liquid at room temperature. From the resolved acid, a number of other chiral species have been synthesized in our laboratory, notably chlorofluoroacetonitrile, HCFClCN, which are sufficiently simple to attempt complete ab initio interpretation of the VOA data.

In the second part of this paper, we report ROA and VCD data of chlorofluoroacetic acid. The observed VOA is interpreted in terms of the atomic displacements which were obtained from the normal-coordinate analyses. Due to the simplicity of the molecule, an assessment of the origin of VOA intensities can be made.

Experimental Section

Racemic chlorofluoroacetic acid (I) (deuteriochlorofluoroacetic acid (II)) was prepared according to published procedures,⁸ by adding chlorotrifluoroethene (Mattheson Gas Co.) to ethanol

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