The crystal chemistry of heptadecyl- and octadecyl-containing n-alkylammonium halides and esters

by

Melanie Rademeyer (Swart)

Dissertation

submitted in fulfillment
of the requirements for the degree

Magister Scientiae

in the

Chemistry

in the

Faculty of Science

at the

Rand Afrikaans University

Supervisor: Prof. G. J. Kruger
Co-supervisor: Dr. D.G. Billing

February 2000
Messages from the universe arrive addressed
no more specifically than
"To Whom it may Concern".
Scientists open those that concern them.

- Norbert Wiener
Acknowledgements

Summary

Opsomming

Section A: Literature review

Chapter 1 Introduction

Chapter 2 Polymorphism

2.1 Polymorphs from crystallization

2.2 Polytypism

2.3 Thermodynamic and kinetic factors influencing polymorphism

2.4 Polymorphic transformation

2.5 Techniques used to study polymorphism

2.6 Conclusion
Chapter 3  Packing of Long chain molecules  

3.1 Hydrocarbon chain packing and subcells  
3.2 Description of subcells  
  3.2.1 Triclinic subcell  
  3.2.2 Monoclinic subcell  
  3.2.3 Orthorhombic ⊥ subcell  
  3.2.4 Orthorhombic // subcell  
3.3 Crystallization  
3.4 Polytypism  
3.5 Odd-even effect  
3.6 Packing in solid solutions  
3.7 Conclusion  

Chapter 4  Waxes  

4.1 Introduction  
4.2 Properties of waxes  
4.3 Classification of waxes  
4.4 A few important waxes and uses  
  4.4.1 Natural waxes  
      Animal waxes - beeswax  
      Vegetable waxes - Carnauba wax  
      Mineral waxes  
      Petroleum waxes  
  4.4.2 Synthetic waxes  


Fischer-Tropsch waxes

4.5 Uses of waxes

4.6 Structure of waxes

4.6.1 Synthetic waxes

Fischer-Tropsch and derived waxes
Paraffinic Fischer-Tropsch waxes
Oxidised Fischer-Tropsch waxes

4.6.2 Natural waxes

Paraffinic waxes
Plant and insect waxes

4.7 Conclusion

Chapter 5  n-Alkanes

5.1 Crystal structure

5.2 Polytypism in n-alkanes

5.3 Thermal behavior

5.4 Structure determinations

5.4.1 Even n-alkanes

5.4.2 Odd n-alkanes

5.4.3 Mixtures of n-alkanes

Solid solution
Fractionated solid solution
Eutectics

5.4.4 Binary mixtures of n-alkanes
Solid solutions 63
Metastable solutions 65
Eutectics 65
5.4.5 Tertiary mixtures of $n$-alkanes 66
5.4.6 Multicomponent mixtures 66
5.5 X-ray diffraction 67
5.6 Molecular modelling 68
5.7 Conclusion 68

Chapter 6 Fatty acids 70
6.1 Occurrence of normal fatty acids in natural products 71
6.2 Crystallography of fatty acids 72
6.2.1 Even saturated fatty acids 73
A-form 74
B-form 75
C-form 78
E-form 79
Phase transitions 80
Crystallization of a specific polymorph 83
6.2.2 Odd saturated fatty acids 84
A'-form 84
B'-form 85
C'-form 87
6.3 Odd-even effect 88
6.4 Conclusion

Chapter 7  n-Alkylammonium halides

7.1 Phase transitions of n-alkylammonium halides
7.2 Structural investigations

7.2.1 Low temperature polymorph - interdigitated phase
    n-Alkylammonium chlorides
    n-Alkylammonium bromides

7.2.2 Non-interdigitated phase
7.2.3 High temperature structures
     DSC investigations

7.3 Conclusion

Chapter 8  Esters

8.1 Methyl esters
8.2 Ethyl esters
8.3 Propyl esters
8.4 Symmetrical esters
8.5 Long chain unsymmetrical esters
8.6 Conclusion

Section B:  Experimental work

Chapter 9  Fatty Esters

9.1 Methyl and ethyl heptadecanoate
   9.1.1 Synthesis
   9.1.2 Crystallization and X-ray diffraction
9.1.3 Thermal measurements 130

9.2 Hexadecyl heptadecanoate and Heptadecyl heptadecanoate 135

9.2.1 Synthesis 139

9.2.2 Crystallization 140

9.2.3 X-ray Powder diffraction 136

Chapter 10  

\textit{n-Alkylammonium halides} 139

10.1 Synthesis 139

10.2 Crystallization 140

10.3 \textit{n-Octadecylammonium bromide} 142

10.3.1 Thermal measurements 142

10.3.2 Single crystal structure determination 144

10.3.3 X-ray Powder diffraction studies 147

10.4 \textit{n-Octadecylammonium chloride} 154

10.4.1 Hot stage microscopy study 154

10.4.2 Powder diffraction study 156

10.5 \textit{n-Octadecylammonium iodide} 164

10.5.1 \textit{n-Octadecylammonium iodide hydrate} 164

10.5.2 Thermal investigations 165

Section C:  

Discussion and Conclusions

Chapter 11  

Discussion and Conclusions 166

11.1 \textit{n-Octadecylammonium halides} 167

11.2 Esters 174
Chapter 12 Future Work

12.1 \( n \)-Alkylammonium halides

12.2 Fatty Esters

References
Acknowledgements

Firstly I would like to thank my promoter, Prof. G. J. Kruger for giving me the opportunity to work with him in the interesting field of crystallography. I want to express my gratitude to him for providing for guidance, encouragement and help during the period I worked with him. I look forward to continue my studies with him.

I would also like to thank my co-promoter, Dr. D.G. Billing for the valuable discussions we had over the past couple of months. I want to thank him for the time he took to familiarize me with the diffractometer at UNISA, and always motivating me by getting excited about chemistry, and particularly crystallography.

I gratefully thank Prof. E.C. Reynhardt at UNISA for allowing me to use the powder diffractometer at his department, and also indirectly introducing me to the field long chain molecules.

Thanks to my husband Hilgard for his support and motivation. Many thanks to my parents for their love and interest in my work. I would not have achieved what I have without your support.

Finally I would like to thank the Lord for giving me the opportunity to attempt to understand a small part of his wonderful creation.
Summary

Molecules containing a long saturated carbon chain are present in many natural and commercial products. Due to the conformational flexibility of the carbon chain, different molecular conformations of these molecules are possible resulting in polymorphism.

The crystal structure of a material greatly influences its chemical and physical properties, leading to different properties for different polymorphs. Designing materials with specific properties requires the understanding of the underlying fundamental parameters and forces influencing the packing of molecules in the crystal.

A thorough literature study was conducted to determine the crystallographic research that has been done long chain compounds. Not only did this literature study lead to the identification of possible research fields, but also provided a solid background concerning the crystallographic behavior of these systems.

In this project we investigated the polymorphism of simple molecules containing a saturated carbon chain with seventeen or eighteen carbons. Two systems are investigated namely n-alkylammonium halides and esters of fatty acids. By varying crystallization conditions different polymorphs of each compound can be obtained. Various experimental techniques were employed to shed light on the structure and packing of the long chain molecules in the different polymorphs.

The crystal structure of the low temperature polymorph of n-octadecylammonium bromide was determined, as well as the cell dimensions of the low temperature form of n-octadecylammonium chloride. The unit cell dimensions of n-octadecylammonium iodide monohydrate was also determined. The structures of the methyl and ethyl esters of n-octadecanoic acid and the symmetrical ester heptadecyl-heptadecanoate was investigated.

In this project a young, dynamic research field was investigated. This led to the identification of other possible fields of study. Because there are not many reports in the
literature on the crystallographic characteristics of these compounds, the evolving of the project required a lot of creativity.
Opsomming

Baie natuurlike en kommersiële produkte bevat verbindings waarvan die molekule 'n lang, versadigde koolstof ketting bevat. As gevolg van die buigbaarheid van die lang ketting is daar verskillende konformasies van die molekules in 'n kristal moontlik. Die tipe verbindings toon dus komplekse polimorfiese gedrag.

Die chemiese en fisiese eienskappe van 'n materiaal word beinvloed deur die kristalstruktuur van die molekules in die materiaal. Om materiale met spesifieke eienskappe te kan ontwerp is dit nodig om te verstaan watter faktore die pakking van die molekules in die kristal beinvloed. Sodoende kan die verlangde struktuur en dus die verlangde eienskappe verkry word.

Om te bepaal watter navorsing reeds in die veld gedoen is, asook om moontlike areas van toekomstige navorsing te identifiseer is 'n deeglike literatuurstudie gedoen. Hieruit is 'n goeie agtergrond verkry oor die kristalografiese gedrag van die lang ketting molekules.

In hierdie projek is die polimorfisme van molekules wat 'n koolstofketting met sewentien of agtien koolstowwe bevat bestudeer. Twee sisteme is bestudeer: \( n \)-oktadekielammonium haliedes en die esters van vetsure. Deur die verbindings te kristalliseer by verskillende temperature en uit verskillende oplosmiddels is dit moontlik om verskillende polimorwe te verkry.

Die kristalstruktuur van die lae temperatuur polimorf van \( n \)-oktadekielammoniumbromied en die eenheidseldimensies van \( n \)-oktadekielammoniumchloried is bepaal. Die eenheidsel dimensies van \( n \)-oktadekielammoniumjodied-monohidraat is ook bepaal. Die strukture van die metiel-en etiel- esters van \( n \)-oktadekanoësuur asook die struktuur van heptadekielheptadekanoaat is bestudeer.
In hierdie projek is nuwe, dinamiese studievelde ondersoek. Dit het aanleiding gegee tot die identifisering van verdere navorsingsmootlikhede asook kreatiwiteit in die ontwikkeling van die projek.
Section A

Literature review
Chapter 1
Introduction

Scientists value the ability to not only explain and understand experimental observations, but also to predict the behavior of novel systems based on previous findings. In most cases the ability to truly understand and predict behavior requires a fundamental knowledge of the properties that influence the behavior.

In this project our aim was to acquire this fundamental knowledge and understanding of the crystallographic and thermal behavior of long chain molecules. Long chain molecules may be defined as molecules exhibiting an approximately cylindrical shape. We narrowed our focus down to simple molecules containing a saturated, normal hydrocarbon chain containing seventeen or eighteen carbon atoms. Functional groups are present only at one end of the molecule, or as an extension of the chain if it is not at the end. Even though these molecules are very simple, it is necessary to obtain a complete understanding of their behavior before more complicated molecules, or systems containing more than one molecule may be considered.

Systems focused on in our investigation include \( n \)-alkanes, fatty acids, fatty alcohols, long chain esters and \( n \)-alkylammonium halides. These molecules occur in many commercial products including cosmetics, pharmaceuticals, detergents and bactericides. Long chain molecules are also constituents of naturally occurring systems like waxes excreted by animals or plants for protection, and biological cell membranes.

The frequent occurrence of long chain molecules indicates the necessity to understand the structural characteristics of these molecules, as the structure influences the properties and thermal behavior. A change in structure may change the physical properties of the commercial product, and thus the product performance.

Our research focused on two areas. Firstly a thorough literature study was conducted, not only to identify possible areas of experimental work, but also to obtain a solid background regarding the behavior of these systems. This literature study did not only
include the systems of long chain molecules that we investigated experimentally, but also other related systems. By considering other systems, one gets familiar with the nomenclature used to describe these systems, and also the general behavior of the long chain molecules. This allows the identification of a particular observation or property as either a global property exhibited by all long chain compounds, or a property dependent on the functionality of the alkyl chain. The comparison of related systems also facilitate the identification of general trends concerning the crystallography and packing of the molecules.

Because long chain molecules are encountered in so many systems, the literature on these compounds was from various disciplines. These fields include, chemistry, physics, biochemistry, biology, food sciences, mathematics and computer science. Aside from the crystallographic experience gained, valuable knowledge of other disciplines was also obtained.

Secondly, our investigation focused on experimental investigation of the structures of certain long chain compounds identified as important from the literature study. This entailed the synthesis, characterization, crystallization and instrumental investigation of the compounds. Various techniques were employed to shed light on the structural and thermal behavior of the chosen compounds. The main techniques used were single crystal X-ray crystallography and powder diffraction. Secondary techniques include hot stage microscopy, differential scanning calorimetry and computational techniques.

The structure of this report is similar to the way the research was conducted. Section A is a summary of the literature available on the structural characteristics of some long chain molecules. Section B reports the experimental work done in our laboratory, and Section C contains a discussion of the results, conclusions, and some ideas for future work.
Chapter 2
Polymorphism

The ability of a substance to exist in more than one crystal structure in the solid state is defined as polymorphism. These different structures originate from different molecular packings in the unit cell. Approximately a third of organic compounds show polymorphism under normal pressure conditions. This phenomenon has been investigated and reviewed by various authors [Bernstein, 1993; Sato, 1993; Threlfall, 1995; Caira, 1998]. Polymorphism may be due to, firstly, different packings of "rigid" molecules relative to each other, or, secondly, due to different molecular conformations, known as conformational polymorphism.

Because the structure of a material influences its chemical and physical properties, polymorphs may differ in solubility, melting point, hardness, density, conductivity, compressibility and chemical reactivity. In order to design materials with specific properties it is important to understand the relationship between the physical properties and the packing of molecules in the crystal. Investigation of polymorphs provides the opportunity to study the effect of change of structure on physical properties, as the only variable is that of crystal structure. Differences between properties of polymorphs must be due to differences in structure, and vice versa, if a property stays unchanged in polymorphs, it indicates a lack of structural dependence of the property.

More than 3000 entries in the Cambridge Structural Database are described as polymorphs of a substance [Bernstein, 1993]. McCrone made the statement that 'Virtually all compounds are polymorphic and the number of polymorphs of a material depends on the amount of time and money spent in research on that compound.' [Bernstein, 1993].

The occurrence of polymorphism complicates manufacturing processes that involve crystallization, heating and compression. Polymorphic transformations of a product could be caused by a change of temperature, milling, drying or by interaction with solvents.
Crystallization plays an important role in the manufacturing of wax, and in many cases the performance of products based on natural fats and waxes may be influenced severely by the polymorphic forms present in the product, and the degree of crystallinity.

In the pharmaceutical industry, the ability of the active ingredient of a drug to crystallize in more than one crystalline state must be determined early in the pre-formulation studies. This ensures that the manufacturing process is well understood, and that there are no surprises. One polymorph of a drug may be absorbed better than others, influencing the bioavailability. Some polymorphs of a drug may be inactive or even toxic.

The tendency of long chain compounds to crystallize in different polymorphs can be attributed to the conformational flexibility as a result of the long chain. Relatively weak intermolecular forces direct the packing of the molecules. The energy difference between two polymorphic forms may be very small causing both polymorphs to form at specific thermodynamic conditions.

An interesting phenomenon is that of global seeding [Bernstein]. Several cases were reported where a less stable polymorph could not be obtained again once a more stable polymorph had formed. The "disappearance" of polymorphic forms can be attributed to seeding of the environment with crystals of the more stable polymorph. This then causes the exclusive crystallization of the stable polymorph due to seeding of solutions by the crystallites.

The rule of close packing was described by Kitaigorodskii [1961]. The sum of the lattice energy and the vibrational energy is the total energy of a crystal. Close packing minimizes the lattice energy, but this packing interferes with the increased vibrational motion at high temperatures. Lattice energy is lost with a less-close packed structure, but entropy can be gained from the increase in symmetry. The importance of close packing results in the majority of organic compounds to crystallize in a few space groups: \( P2_1/c, P1, C2/c, P2_1, P2_12_12_1 \). The result of both close packing and vibrational requirements is that it is common for a polymorphic system to exist in a monoclinic...
form at low temperatures and transform to an orthorhombic form at higher temperatures.

2.1 Polymorphs from crystallization

Factors that influence the polymorphic behavior during the crystallization of a substance include the solvent, temperature, supersaturation, cooling rate, pressure and the presence of impurities. Small changes in these parameters can cause a different polymorph to be obtained. Even though thermodynamic conditions may predict the crystallization of a certain polymorph, seeds of other polymorphs in the environment may dominate, and cause a thermodynamically less stable polymorph to form.

Nucleation is the main factor determining the crystallization of different polymorphs. If the nucleation for the less stable polymorphs is kinetically faster, this modification will form despite it's lower stability.

Even though supersaturation plays an important role in the crystallization of specific polymorphs, the dominant factor determining which polymorph forms is the solvent. The role of the solvent is kinetic, in that the solvent may retard growth by selectively adsorbing on some faces of certain polymorphs. This may cause the less stable polymorphs to crystallize instead of the thermodynamically stable one. Over a long period of time, the unstable form may revert to the stable polymorph by solution mediated transformation. Solvent parameters that may influence the polymorphism include solubility of compound in solvent, viscosity, and solute-solvent interactions [Sato, 1993]. Pseudopolymorphs are formed when solvent molecules are incorporated in the crystal structure. Pseudomorphosis is the loss of solvent from a crystal when it is removed from the mother liquor.

2.2 Polytypism

Polytypism can be described as one-dimensional polymorphism. This phenomenon is caused by different stackings of the same lamella of long chain molecules [Threlfall, 1995]. In two dimensions the unit cells are the same, but in the third dimension the unit cell is an integer multiple of a mutual unit. This type of polymorphism is
commonly found when the interlamellar forces are weak, allowing different stackings of layers.

2.3 Thermodynamic and kinetic factors influencing polymorphism

In order to obtain the required polymorphic form optimal conditions for crystal growth and possible transformation pathways must be determined [Sato, 1993]. This can only be done once the thermodynamic behavior of the system is understood.

The formation of polymorphs is controlled by the energy relationship $G = H - TS$, where $G$ is Gibbs energy, $H$ enthalpy, $S$ entropy and $T$ the temperature. Thermodynamic stability of polymorphs can be compared by measuring melting point and solubility, and combining the data with information on phase transformation [Sato, 1993]. Polymorphic forms with higher Gibbs energies are less stable and have lower melting points and higher solubilities.

At specific thermodynamic conditions, only one polymorph is stable. This however, does not mean that the stable polymorph is exclusively obtained at a specific temperature and pressure - due to rapid nucleation other metastable polymorphs may form despite their instability. The rate of transformation of the metastable polymorph to the stable form may be very slow, causing these metastable forms to seem stable.

According to Ostwaldt's law of stages [Caira, 1998] it is possible to obtain all possible polymorphs from a solution at different times of crystallization: the form that crystallize first from a supersaturated solution is the thermodynamically least stable, most soluble polymorph. This polymorph dissolves and transforms into a more stable polymorph. This process repeats itself until only the most stable, least soluble polymorph exists. The transformation of one polymorph to another is generally one of two types: enantiotropic or monotropic.
2.3.1 Enantiotropic transformation

In Fig. 2.1: Relationship between Gibbs energy and temperature for two polymorphs related by a reversible, enantiotropic transformation [Garti and Sato, 1988].

In Fig. 2.1 the Gibbs energies of two substances A and B, G(A) and G(B) cross at a specific temperature $T_0$. If the polymorphic transformation is reversible, the exclusive crystallization of the more stable form occurs at any temperature.

If the polymorphic transformation of both A to B ($T > T_0$) and B to A ($T < T_0$) is irreversible (Fig. 2.2) both polymorphic forms can occur at temperatures where metastable forms of the less stable polymorph can exist. If the transformation of A to B occurs at a temperature below the melting point of B, B crystallizes from the melt. If the transformation occurs above the melting point of B, both A or B may crystallize. Usually the high temperature form is obtained from the melt, but either A
or B can crystallize from solution, depending on the specific environmental conditions.

2.3.2 Monotropic transformation

![Diagram of Gibbs energy and temperature for monotropic transformation](image)

**Fig 2.3:** Relationship between Gibbs energy and temperature for a monotropic transformation [Garti and Sato, 1988].

If the curves of $G(A)$ and $G(B)$ cross above the melting temperatures of both A and B, both forms may crystallize, and the outcome of the crystallization process is determined by a competition between the crystallization and transformation processes. The higher melting form is the thermodynamically most stable form.

2.4 Polymorphic Transformation

Polymorphic transformations occur through four mechanisms: solid state, solution mediation, melt mediation and interface mediation [Sato, 1993].

If the crystallization from solution is slow, the crystallization process approaches equilibrium. This process is known as solution mediated transformation and leads to the formation of the more stable form at the expense of the less stable form. The force driving solvent mediated transformation is the difference in solubility of polymorphs. The rate of transformation increases with increasing solubility, since both the rates of dissolution and growth are raised. Impurities influence the rate of solution mediated transformation. An example is the effect that surfactants have in the transformations of $n$-octadecanoic acid (stearic acid) [Garti and Sato, 1986]. Interactions between solvent, solute and surfactant cause the retardation of transformations, primarily because of adsorption on the less stable forms, and prohibition of the stable form.
Inclusions of mother liquid in the crystal and adsorption of solvent on the surface also mediates polymorphic transformations.

Interface mediated transformation is the growth of a new polymorph across the interface between single crystals of different polymorphs via mass transfer. The difference between solid-solid transformation and interface mediated transformation is the presence of a microscopic layer of solution at interface with interface mediated transformation.

If a certain polymorph is melted, and another polymorph crystallizes from the liquid, the process is called melt-mediated transformation.

Generally solution, melt and interface mediated transformations of polymorphs are much faster than solid-solid transformations since steric hindrance in a solid-solid transformation results in a high activation energy.

If different conformers of a molecule crystallize, the phenomenon is known as conformational polymorphism.

2.5 Techniques used to study polymorphism

2.5.1 Hot stage microscopy (HSM)

This method is used to detect the existence of polymorphism by the observation of a solid-solid transformation. A pseudopolymorph is indicated by the evolution of gas bubbles. Very little material is required for this technique. Phase transitions not observed by DSC are sometimes observed by HSM.

Besides the determination of melting points and transition temperatures, it is possible to video record thermal events. Changes in a sample are often only noticed after it has occurred. By video recording the event, it is possible to replay and observe the changes again.
2.5.2 Electron diffraction

Due to the difficulty of obtaining single crystals of long-chain compounds suitable for structure determination using single crystal X-ray diffraction, attention has moved to the employment of electron diffraction to obtain data from small microcrystals.

Dorset has performed various structure determinations using microcrystals or epitaxially orientating long chain molecules on a crystalline substrate [Dorset, 1995].

If a long chain substance is crystallized from solution or from the melt, the molecules are aligned perpendicular to the surface on which it crystallizes. When these crystals are studied by electron diffraction, the electron beam is projected along the molecular axis, onto a unit cell with one long dimension. This may present problems if the thin plates are slightly bent. When investigating long chain molecules with the electron microscope, it is sometimes desirable to rather project the electron beam perpendicular to the axis of the molecule. This orientation facilitates the determination of the two short unit cell dimensions. A sample with the molecules parallel to the surface of crystallization can be obtained by epitaxially orientating the molecules on a substrate. The lattice of the substrate directs the orientation of the molecules. An organic (for example potassium hydrogen phthalate) or inorganic (for example KCl or KBr) substrate may be used.

Molecules can be directed epitaxially in two ways: from the vapor or from the melt. To grow a layer from the vapor [Zhang and Dorset, 1989], vapor is deposited onto the substrate in a vacuum, with the lattice of the substrate directing the packing of molecules. The organic film is removed from the substrate by immersing it in water, causing the substrate to dissolve. After drying the film, the sample is ready for investigation under an electron microscope.

It is difficult to obtain a good quality single crystal of a solid solution of two components. By epitaxially orientating a solid solution from the melt of the two components a sample suitable for the electron microscope can be prepared. Various methods of sample preparation may be used. The preparation generally entails the melting of the sample and the substrate together, followed by the crystallization of the
nucleating substrate, and then the crystallization of the sample onto the crystalline substrate. If the oriented molecules are not hydrophilic, the substrate may be removed by immersing the sample in water. Otherwise it is necessary to sublimate the substrate.

Electron diffraction investigates a small area of the sample. From the diffraction pattern the unit cell dimensions and crystal structure may be determined employing various computational techniques.

2.5.3 Thermal methods of analysis

Differential Scanning Calorimetry (DSC), thermogravimetric analysis (TGA) and differential thermal analysis (DTA) are methods used to investigate the polymorphic behavior of a substance as a function of temperature. The determination of the stoichiometry of a pseudopolymorph is facilitated by TGA. This allows the calculation of the percentage weight loss with temperature [Caira, 1998].

During a phase change, heat is emitted or absorbed. DTA compares the temperature of a sample with that of a reference material as a function of temperature. Where hot stage microscopy is a qualitative, visual technique, DSC, DTA and TGA provide quantitative measurements that can be used to calculate enthalpies of thermal events. In a plot of temperature (T) vs. heat flow, endothermic peaks correspond to desolvation of pseudopolymorphs, or phase transitions for polymorphs, and exothermic peaks correspond to crystallization or decomposition. In a DSC scan, the difference in energy input into a sample and reference material is plotted as a function of temperature. From these traces enthalpy changes corresponding to transitions can be determined. DSC measurements and the complimentary hot stage microscopy data enables the determination of phase diagrams for mixtures of substances.

Even though thermal analysis techniques are base on readily understandable principles, the environment of the sample may also influences its thermal behavior. The shape of thermograms obtained is dependent on heating rate, crystallite size, packing of the sample in the sample holder and the atmosphere. The thermal history of a sample will also influence its thermal behavior, and subsequent scans may differ.
During storage a sample may undergo a polymorphic transformation, and the period elapsed from preparation to thermal measurement can influence the thermal analysis results.

Heating of the sample at the right rate is crucial – a polymorph may show a transition to a higher temperature phase when heated slowly, but overshoot and melt at a higher heating rate. Depending on the complexity of the polymorphic system, a whole set of thermal peaks may be observed. Several solid-state transitions may occur if liquid crystals form.

Interpretation of thermal measurements has been facilitated by Burger's rules: [Turkulov, 1995]
- when a substance exhibit an endothermic transition at a specific temperature on heating, there must be an enantiotropic transition at or below that temperature
- when a substance exhibit a exothermic transition, then the transition point must be above that temperature, or a monotropic transition is present

Profiles present in DSC scans can sometimes be generalized. For example, a large endotherm followed by a smaller melting endotherm is characteristic of the onset of free rotation in organic molecules (as seen for long-chain compounds).

2.5.4 X-ray diffraction

Single crystal X-ray diffraction

The primary technique to study polymorphism is single crystal X-ray diffraction. This method permits the determination of atomic positions in the unit cell, enabling the calculation of bond lengths, bond angles, torsion angles and conformation of the molecule. The packing of molecules in the different polymorphic forms is established, facilitating the comparison of different polymorphic crystal structures.
Fig 2.4: Bragg’s Law

In Fig 2.4, the difference in path length between the waves scattered at B and D is equal to $AB + BC = 2d \sin \theta$.

Bragg’s Law describes the requirement for diffraction

$$2d \sin \theta = n \lambda$$

where $d$ is the spacing between the layers of atoms, $n$ is an integer value, and $\lambda$ is the wavelength of the X-ray radiation. Only certain values of $\theta$ lead to diffraction of the X-ray beam.

In the single crystal technique, a single crystal is placed in the path of a X-ray beam, and the intensities of diffracted beams are counted. From the diffraction pattern the three dimensional structure of the compound can be determined. Standard techniques include direct methods for phase determination and least-squares procedures for refinement.

Many polymorphic forms exhibit such small changes in crystal structure, that single crystal X-ray crystallography is the only method available to identify these polymorphs. This method aids in the interpretation of results obtained via other techniques.
Low temperature data recordings retard or inhibit loss of solvent molecules from the crystal lattice, and are used to determine the structure of pseudopolymorphs that contain solvent molecules exhibiting excessive thermal motion and disorder.

**X-ray powder diffraction**

Pertaining to the difficulty sometimes experienced in obtaining single crystals of polymorphic forms, the technique of X-ray powder diffraction can unequivocally indicate the non-equivalence of crystal structures. A powder diffraction pattern serves as a "fingerprint" of polymorphs, and can be used to prove the isostructurality of polymorphs of similar compounds.

In powder X-ray diffraction, a powder containing many randomly orientated small crystallites diffracts X-rays. The three dimensional information is compressed into one dimension. The powder pattern can be considered as a fingerprint of a crystalline substance, i.e. different polymorphs of the substance.

However, various problems may be experienced in the preparation of the sample. Grinding of the sample may cause a polymorphic transition, and the effect of preferred orientation can be disastrous, causing the intensities of certain reflections to be much more intense than the rest of the reflections. The various techniques to minimize preferred orientation depend on the type of crystallites present. The sample may be sprinkled onto a glass slide covered with a layer of petroleum jelly, but this does not help if the crystallites are flat plates. To minimize the effect of preferred orientation for flat plates, a capillary sample holder can be used, but this may not work for needle shaped crystallites.

The effectiveness of analytical methods used to study polymorphism is optimized when the techniques are used in combination.
Structure determination from powder patterns

Structure determinations from powder diffraction data are performed more and more frequently. Structure factors can be extracted from diffraction data employing the methods of Le Bail or Pauwley. Refinement of the structure is then performed by the same standard techniques used for single crystal data.

If an experimental powder pattern has been indexed, and the unit cell dimensions and space group are known, the Le Bail method for extracting intensities of overlapping peaks can be applied. The calculated profile is compared to the measured profile and a least square refinement is performed. The lattice parameters, peak widths and peak shapes are allowed to vary. The intensities are, however, not known. At the beginning of the Le Bail extraction, the overlapping peaks are assigned equal intensities. After the first cycle, the intensities will not be equal anymore. This procedure is repeated until the extraction converges.

Rietveld method

The structural model obtained from refinement of the extracted structure factors, can then be refined using the Rietveld method.

In a stepped scan powder pattern, information can be obtained from every point in the pattern, even if the information is such that no intensity is obtained at that step. Rietveld [1969] proposed mathematical procedures to extract the maximum amount of information from a powder pattern using a computer. In what has become commonly known as the “Rietveld Method”, the best fit between a calculated and an experimental powder diffraction pattern is obtained by least square refinements of various parameters.

This method is a structure refinement method, not a structure solution method. Since unit cell dimensions determine the position of peaks, and atomic co-ordinates determine the intensities at different angles, a relatively good starting model is required before the start of refinement. The refinement also takes into account various structural and instrumental parameters and characteristics of the sample. Refinable
parameters include unit cell dimensions, scale factors, zero-point correction, temperature factors, peak shape functions, preferred orientation, asymmetry of peaks, absorption, atomic parameters, and background functions. Refinable atomic parameters are the site occupancy of an atom, fractional co-ordinates in the unit cell and thermal vibration parameters.

If extensive overlap of diffraction peaks occur, it is not possible to obtain the integrated intensity of every reflection.

With every step, \( i \), in a powder diffraction pattern, an intensity \( y_i \) is associated. The desired best fit is the best least-squares fit of all the \( y_i \) values together. In the least-squares refinement the quantity \( S_y \) is refined:

\[
S_y = \sum w_i (y_i - y_{ci})^2
\]  

(1)

With

\[
w_i = \sigma(1/\sigma(y_i))
\]

\( y_i \) = observed intensity at the \( i \)th step

\( y_{ci} \) = calculated intensity at the \( i \)th step

The calculated intensity at every step \( i \), \( y_{ci} \) is determined from the \( |F_{hkl}|^2 \) values obtained from the structural model by summation of contributing Bragg reflections and the background [Giacovazzo, 1991].

\[
y_{ci} = s \sum K L K |F_K|^2 \phi (2\theta_i - 2\theta_K) P_K A + y_{bi}
\]

(2)

where \( K \) indicates the indices \( h, k, l \).

\( s \) represents the scale factor

\( L_K \) contains the Lorentz, multiplicity and polarisation factors

\( \phi \) is a function describing the reflection profile

\( P_K \) is a preferred orientation function

\( A \) represents absorption

\( F_K \) is the structure factor of the \( K \)th Bragg reflection

and \( y_{bi} \) is the background intensity at step \( i \)
The result of the least-squares calculation is a set of equations containing derivatives of the calculated intensities, $y_i$. The intensities are derived with respect to every parameter that is refined. A normal matrix is obtained that contains elements $M_{jk}$ described by

$$
M_{jk} = -2 \sum_i w_i \left[ (y_i - y_{ci}) \frac{\partial^2 y_{ci}}{\partial x_j \partial x_k} - \left( \frac{\partial y_{ci}}{\partial x_j} \right) \left( \frac{\partial y_{ci}}{\partial x_k} \right) \right]
$$

where $x_j$ and $x_k$ are variable parameters. If $m$ parameters are refined, a $m \times m$ matrix is obtained and inverted. By an iterative procedure the shifts ($\Delta x_k$) in parameters are calculated and applied to the starting parameters obtaining a possible improved model.

$$
\Delta x_k = \sum_j M_{jk}^{-1} \frac{\partial S}{\partial x_j}
$$

The cycle is repeated and the new calculated shifts are applied to the improved parameters. The desired end result of refinement is the determination of the global minimum. In order to avoid false minima, a good starting model is necessary. It can easily happen that a local minimum instead of the global minimum is obtained from refinement. This is difficult to avoid, but one possible solution is to try various starting models and to observe if the same minimum is obtained.

In the Rietveld method more than one phase can be refined simultaneously. This facilitates the refinement of a sample containing more than one polymorphic form of a substance.

The background can be refined using various models. The user can supply values of the background at different angles. If the background is relatively flat, it can be approximated by linear interpolation between points specified by the user. Thirdly the background can be described by a polynomial function. If this function is used, the operator must provide a starting origin. This is probably the best option if the
background is not flat, but consists of bumps. In equation (2), $\phi$ represents various instrumental and sample parameters. These include sample absorption, asymmetry of the peaks and sample displacement.

Various functions describing the profile of peaks can be specified by the user depending on the shape of the peaks. Popular functions include pseudo-Voigt functions, the Pearson VII and split Pearson VII functions, Gaussian and Lorentzian functions. Many peak profiles can not be modelled acceptably by use of only broad Gaussian or narrow Lorentzian functions. This lead to the introduction of hybrids of these functions to model intermediate peaks shapes. The Voigt function ranges from pure Gaussian to Lorentzian, and is described by equation (3).

\[
V(x, \Gamma_L, \Gamma_G) = L \left( x / \Gamma_L \right) * G \left( x / \Gamma_G \right) \tag{3}
\]

where

- $L$ = Lorentzian function with a full-width-at-half-maximum (FWHM) of $\Gamma_L$
- $G$ = Gaussian function with a FWHM of $\Gamma_G$
- $x = \Delta 2\theta$

If the pseudo-Voigt function is used, the ratio of Gaussian and Lorentzian character is specified and refined by use of a mixing parameter indicating the fraction of each function applied.

The shape of the symmetric Pearson VII function also ranges from Gaussian to Lorentzian. The function is described by equation (4).

\[
I = I_0 / (1 + ax^2)^m \tag{4}
\]

with

- $a = (2^{1/m} - 1)/\Gamma^2$; $\Gamma$ is the FWHM and $m$ a shape factor determining the rate of falling of the tails of the peak

The split-Pearson VII function can be used to successfully model asymmetric peak shapes. In this function the peak is split into two separate functions with each half possessing a different ratio of Gaussian and Lorentzian character.
Fig 2.5: The split-Pearson VII function used to model the two halves of the peak with different Pearson VII functions.

With increasing $2\theta$ angle the diffraction peaks become broader. $\Gamma$, the angular dependant breadth at FWHM has been modelled using the following function

$$\Gamma^2 = U \tan^2 \theta + V \tan \theta + W$$

where $U$, $V$ and $W$ are parameters that may be refined.

The structural model may also be corrected for preferred orientation. The correction can be made by applying a correction function depending on the acute angle $\phi$ between the preferred orientation plane and the diffraction plane $k$: [Giacovazzo, 1991].

$$I_k(\text{corr}) = I_k P_k(\phi)$$

In this equation, $P_k$ can be Gaussian

$$P_k(\phi) = \exp(-p\phi^2) \quad \text{or} \quad P_k(\phi) = \exp[p(\pi/2 - \phi^2)]$$

or contain trigonometric functions

$$P_k(\phi) = (p^2 \cos^2 \phi + \sin^2 \phi/p)^{-3/2}$$
The structure factor $F_K$ in equation (2) is determined by the equation

$$F_K = \sum_j N_j f_j \exp\left[2\pi i (hx_j + ky_j + lz_j)\right] \exp[-M_j]$$

with $h, k, l$ the Miller indices

$x_j, y_j, z_j$ the fractional co-ordinates of atom $j$

$$M_j = 8\pi^2 u_j^2 \sin^2 \theta / \lambda^2$$

$u_j^2$ is the root-mean-square thermal displacement of atom $j$ in the direction parallel to the diffraction vector.

and $N_j$ is the site occupancy of atom $j$.

The sequence in which parameters are refined can determine whether the refinement is successful or not. If unstable parameters are refined too soon, it may cause the refinement to diverge. A good strategy involves the refinement parameters in approximately the following order: scale factor, sample displacement, background, lattice parameters, second background variable, $W$, $x, y, z, N'$s, $B'$s, $U$ and $V$ [Young, 1995].

The use of graphical criteria of fit is important to monitor the refinement process. Certain errors will be clearly visible in a difference plot between the calculated and experimental diffraction pattern. Problems regarding the unit cell parameters scale factor and contamination will not be easily identified if the criterion of fit used is purely mathematical.

Numerical criteria of fit are, however, important. It gives an indication on the progression of the refinement process after each cycle. Several $R$-values, related to the $R$-value used by single crystal crystallographers may describe the goodness of fit. These include the ‘$R$-structure factor’:

$$R_F = \frac{\sum |(I_K('obs'))^{1/2} - (I_K('calc'))^{1/2}|}{\sum (I_K('obs'))^{1/2}}$$
'R-Bragg factor':

\[ R_B = \frac{\sum |y_i('obs') - y_i(calc)|}{\sum y_i('obs')} \]

'R-pattern':

\[ R_p = \frac{\sum |I_K('obs') - I_K(calc)|}{\sum I_K('obs')} \]

'R-weighted pattern':

\[ R_{wp} = \left( \frac{\sum w_i(y_i('obs') - y_i(calc))^2}{\sum w_i(y_i('obs'))^2} \right)^{1/2} \]

The 'R-Bragg' and 'R-structure' factors are similar to R-factors appearing in single crystal crystallography. These values are, however, calculated from intensities determined from the structural model, and as a result biased towards the model. The weighted R-factor best reflects the progress of the refinement procedure because the numerator in the equation is minimised. Another indication of the progression of refinement can be obtained from the 'goodness of fit', S.

\[ S = \left[ \frac{S_y}{N-P} \right]^{1/2} = R_{wp}/R_e \]

where

\[ R_e = 'R-expected' = \left[ \frac{(N-P)/\sum w_i y_{oi}^2}{(N-P)/\sum w_i y_{oi}^2} \right]^{1/2} \]

and \( N \) is the site occupancy multiplier,

The required S value is approximately 1.3. A larger value may indicate an error in the structural model.

General guidelines concerning the different steps in Rietveld refinement have been formulated by the International Union of Crystallography Commission on Powder Diffraction [McCusker et al, 1999].
2.5.5 Other techniques

The Solid State Nuclear Magnetic Resonance (NMR) spectrum contains information on the chemical environment of atoms. Differences in the packing of molecules can be identified, and the hydrogen bonding networks may be characterized. This technique lends itself to the identification and comparison of polymorphs of a compound.

Solid-state Infrared (IR) spectroscopy is a technique used to distinguish polymorphs and pseudopolymorphs. Differences in packing of molecules result in differences in hydrogen bonding that is manifested in IR spectrums by frequency shifts and splitting in, for example, N-H and O-H peaks. IR spectra can indicate the existence of a different polymorphic form of a substance, and the necessity to investigate the system using techniques like single crystal X-ray crystallography. The effectiveness of analytical methods used to study polymorphism is optimized when the techniques are used in combination.

2.6 Conclusion

The need to design materials with specific properties has greatly increased the interest in the investigation of polymorphism because the properties of materials are determined by the crystalline assembly of molecules in the solid state.

Lack of knowledge of fundamental parameters influencing crystal packing has hampered the development of crystal engineering and design. There is clearly a need for the systematic investigation of the forces directing the crystallization of polymorphs of a system, before the properties of the system can be understood. A broad array of analytical techniques can be employed to study the interesting phenomenon of polymorphism. The final goal would be the ability to predict the polymorphic form of the compound from the thermodynamic and physical conditions of crystallization.
Chapter 3

Packing of long chain molecules:

The term "long chain molecule" will be used to describe a molecule containing a functional group attached to an alkyl chain (see Fig 3.1). In this report, only simple, saturated straight alkyl chains are considered. Many of the concepts, however, are also applicable to unsaturated chains.

![Alkyl chain](image)

Terminal functional end group

Fig 3.1: Schematic representation of a long chain molecule

These types of molecules have special properties derived from the packing of the functional groups and the long chain. Long chain compounds include normal alkanes, alcohols, fatty acids, n-alkylammonium halides and long chain esters.

In the solid and liquid state, long chain molecules generally have their axes aligned. In a crystal the chain molecules crystallize in layers, with their terminal groups forming a plane. The structure is formed by association of these layers by symmetry operations.
Various ways of stacking lamella are possible. In Fig 3.2 some of the stacking possibilities are indicated.

Fig 3.2: Packing of aliphatic molecules: (a) Vertical chains of \( n \)-alkanes leading to orthorhombic unit cell (b) V-shaped packing of \( n \)-alkanes resulting in orthorhombic unit cell (c) tilted chains of \( n \)-alkanes resulting in a monoclinic unit cell (d) interdigitated packing (e) dimers with tilted chains parallel (f) dimers with chains vertical (g) dimers with parallel tilted chains and layers related by a two fold rotation axis (h) chains with two aliphatic parts, for example esters.

The fundamental starting point to consider packing of long chain molecules in the crystalline state, are the \( n \)-alkanes. In these molecules all the carbon atoms lie in a plane, resulting in a flat zig-zag. The distance between two alternating carbon atoms is 2.54 Å, and the angle between three consecutive carbon molecules in the zig-zag chain tends to 112°. This extended conformation of the chain has the lowest energy and is called the “\textit{trans}” conformation.
Fig. 3.3: Low energy trans conformation for n-alkanes

This conformation may be distorted if substituents are present. It was shown [Kitaigorodskii, 1961] that the melting points of various terminal functionalized long chain molecules converge to a single value, that of polyethylene. Thus, the more carbon atoms there are in the long chain, the smaller will the effect of terminal substituents be, with the properties tending to those of polyethylene. The packing of molecules containing a large number of CH2 groups will be similar to that found for n-alkanes.

3.1 Hydrocarbon chain packing and subcells

Despite the many possible terminal functional groups of long chain molecules, only a limited number of n-alkyl packings are possible. It was recognised by Vand [1953] that long hydrocarbon chains packed in a parallel array would contribute a periodic structure inside the unit cell, and he proposed the concept of a subcell. The best method to describe the packing of the hydrocarbon part of long-chain aliphatic molecules is to use a subcell that corresponds to the smallest repeat unit in the hydrocarbon layer. The subcell describes the relationship between neighbouring hydrocarbon chains, facilitating a distinction between the hydrocarbon parts of polymorphic forms. By repeating the subcell laterally, the structure of the hydrocarbon chain part can be obtained. Three axes describe the subcell: \( a_s \), \( b_s \) and \( c_s \), with the \( c_s \) axis in the lateral direction. The nomenclature commonly used for a subcell is a letter indicating the symmetry (T for triclinic, M for monoclinic, O for orthorhombic and H for hexagonal), followed by a symbol indicating whether the planes formed by the zig-zag of carbon molecules is perpendicular (\( \perp \)) or parallel (\( // \)) [Segerman, 1965].
3.2 Description of subcells

3.2.1 Triclinic-T// Subcell:

This subcell contains two CH$_2$ groups with space group P1. The zig-zag planes of all the chains are parallel, but neighbouring chains have opposite C-C bond directions relative to a plane normal to the $c_s$ direction.

3.2.2 Monoclinic-M// Subcell:

In the monoclinic subcell all the chains are parallel as in the T// subcell, but the neighboring chains all have the same C-C bond directions relative to a plane normal to the $c_s$ direction.
3.2.3 Orthorhombic-\(0\perp\) Subcell:

Two orthorhombic hydrocarbon subcells are possible: the \(0\perp\) and the \(0\perp'\). Four \(\text{CH}_2\) groups are contained in the cells, with space group \(Pbnm\). In both orthorhombic subcells, the chain planes have two orientations, perpendicular to each other. Of the two, the \(0\perp\) subcell is most commonly displayed. The main difference between the \(0\perp\) and the \(0\perp'\) subcells is an inversion of the \(a_s\) and \(b_s\) axes.

3.2.4 Orthorhomic-\(0//\) Subcell:

Two orthorhombic subcells with the zig-zag carbon planes parallel are found, \(0//\) and \(0//'\). There are eight \(\text{CH}_2\) groups in the \(0//\) subcell with space group \(B22_12\). The space group of the \(0//'\) subcell is \(Pma2\).
3.3 Crystallization

Generally, long chain molecules tend to grow in thin, flat plates, with limited crystal growth in the direction of the molecular long axis, resulting in deformable crystals and, very often, twinning across the plane of the crystal.

3.4 Polytypism

Long chain molecules form plate-like crystals with lamellar structures - one layer stacks above the other in a direction normal to the flat surface of the plate. When two or more orientations of layer stacking is possible, different crystal structures may be formed due to the different layer stacking. This change in structure in view of different layer stacking is called “polytypism”.

Fig 3.4: Polytypism exhibited by lamella containing tilted chains

Polytypism can be described as one-dimensional polymorphism. It is often found that long chain molecules are packed with the molecular axis inclined relative to the lamellar layer, resulting in two possible stacking modes: one in which two layers are stacked with the same orientation, and one where the one layer is turned at 180° relative to the other [Kobayashi, 1993]. These two orientations of layers can be described by A and V, and the possible polytypes are described by \((A_p V_q)\), where \(p\) and \(q\) denotes the number of successive layers with that particular orientation. The monoclinic form generally found is one of the extreme cases (A) or (V). Another polytype that belongs to an orthorhombic system is formed by alternation of the
layers, \( (A\forall) \). Both these structures are formed by the same molecular layers, but differ in the structure of the lamellar interface.

The crystal and physical properties of functionalized hydrocarbons differ widely, despite the fact that the basic building blocks are the same. These properties can be influenced by the number of carbon atoms in the chain, the parity of the number of carbon atoms in the chain, and the different end functional groups.

3.5 Odd-even effect

One of the most prominent features of aliphatic molecules is the so-called "odd-even effect". This refers to the differences in packing and properties of \( n \)-alkanes and \( n \)-alkane derivatives with an odd number or an even number of carbon atoms in the alkyl chain. The symmetry of an \( n \)-alkane molecule with an odd number of carbon atoms is \( mm \), whereas the symmetry of an even \( n \)-alkane molecule is \( 2/m \). An uneven molecule keeps one mirror plane in the crystal lattice, and an even molecule keeps its center of inversion [Kitaigorodskii, 1961].
Only even \( n \)-alkanes have the symmetry required to have equivalent packing of end-groups when the molecules are tilted. If an odd numbered \( n \)-alkane is tilted, and one end is in a low energy position, the other end is forced into a high-energy position [Broadhurst, 1962].

![Diagram](a) Packing of tilted, even \( n \)-alkanes (b) Packing of tilted, odd \( n \)-alkanes

As a result, odd \( n \)-alkanes only pack with molecules perpendicular to the layers formed by the terminal methyl groups and crystallize in the orthorhombic modification [Retief, 1978]. For molecules containing an even number of carbon atoms, the chains can either be perpendicular or tilted relative to the layers, forming either an orthorhombic or monoclinic modification.

In the solid state, van der Waals forces direct interaction between adjacent hydrocarbon chains. This force has the least impact in directing association of molecules. If terminal functional groups are present, ionic forces and hydrogen bonds may be the major forces directing the packing. The packing of molecules is influenced by two factors: the force between the end groups in a layer, and the van der Waals force between the hydrocarbon parts of layers. These two forces contribute to the energy of the lattice, and their relative strength determines the crystal structure. The resulting structure is a compromise between attaining the highest symmetry in the crystal, and the tendency towards close packing [Retief, 1978]. Two conformations can have similar energies, and the preferred structure is then determined by external factors like thermodynamic crystallization conditions.
For \( n \)-alkanes the directing force between methyl end groups is relatively small, causing it to have little effect on the structure. This leads to polytypism where layers of molecules are stacked in different ways for polytypes of a compound. The sideways force in lamella between molecules is much stronger.

A geometrical analysis of the possible structures for aliphatic molecules based on close packing was presented by Kitaigorodskii [1961]. If it is assumed that the hydrocarbon chains are of infinite length, the end group effects can be ignored. The closest packing is obtained if an H atom in one molecule enters into the cavity formed by three H atoms of a neighboring molecule.

The close packing theory is insufficient in describing the packing of chain molecules containing functional groups capable of forming hydrogen bonds. The association of molecules may be different because hydrogen bonds have higher energies than van der Waals bonds. Two molecules may combine via these functional groups to form dimers, with the two molecules related by a center of inversion or a two-fold rotation axis.

Under certain thermodynamic conditions, only one association of long chain molecules is an equilibrium state [Vainstein, 1966; Segerman, 1965]. But crystals containing different assemblies of molecules can be stable if kinetic factors are important.

It is assumed that the molecule starts rotating around its long axis at high temperatures. This high temperature modification is commonly called the ‘rotator phase’. The structural character of the rotator phase has been investigated by various researchers [Craevich et al, 1985]. In this modification the chain molecules possess a high degree of disorder – not only due to rotation. Evidence was given for rigid body longitudinal displacement of molecules as well as defects (kinks in molecules) in the rotator phase. The longer the chain molecule, the larger the disorder becomes at a certain temperature. The disorder is also a function of temperature – higher disorder is exhibited at higher temperatures. Hexagonal or monoclinic packing is commonly observed for this phase. Hexagonal packing is the best close packing that can be obtained if the cross-section of a molecule is almost circular. This phase resembles a
liquid crystal, and the behavior is displayed over a certain temperature range. If functional groups are present, this transformation from the crystalline state to the liquid crystal can be described as partial melting of the alkyl chains. Two types of liquid crystals are found: nematic and smectic [Vainshtein, 1966]. In both types the chains are parallel, but in the nematic state, the chains do not form a layered structure. In the smectic state, the chains form layers, with a higher degree of order than found in the nematic state. The smectic state occurs at a lower temperature than the nematic state, another indication that it possesses lower energy.

![Liquid crystalline states](image)

*Fig 3.7* Liquid crystalline states: (a) partial melting of hydrocarbon chain (b) smectic liquid crystal (c) nematic liquid crystal

3.6 Packing in solid solutions

For chain molecules to form a solid solution certain requirements must be fulfilled. Kitaigoroskii [1961] described these requirements in terms of symmetry. The molecules constituting the solid solution must be of similar shape and size, and isomorphous. This requires the molecules to belong to the same space group and contain the same number of molecules in the unit cell. If constituents in a mixture differ in these parameters, the end group packing is disturbed. This prevents the crystallization of layers with the chains tilted relative to the end groups - the only possible packing is orthorhombic with the chains perpendicular to the end group layers. Because odd and even molecules of compound do not belong to the same space group, a continuous solid solution cannot be obtained for an odd-even mixture. Kitaigorodskii also stated that addition of solute A to solvent B must not rise the symmetry of B. Addition of A must either leave the symmetry of B unchanged, or lower it.
These symmetry-based rules of Kitaigorodskii have been proven invalid in a few instances. For example, some solid solutions exhibit a higher orthorhombic symmetry than the triclinic components. The formation of a stable solid solution between odd and even compounds has also been indicated [Dorset, 1987].

3.7 Conclusion

The packing characteristics described above apply not only to n-alkanes, but also to normal derivatives of n-alkanes. The presence of functional groups may, however, be the predominant factor influencing the packing.

General trends in packing of molecules can be identified for long chain molecules:
- Molecules tend to pack with the chain axis parallel forming layers
- The crystal is build up by stacking of the layers
- This trend results in the formation of crystals in the shape of thin plates
- Due to the conformational freedom of the long chain polymorphism is exhibited by these molecules.
Chapter 4

Waxes

4.1 Introduction

The use of wax is as old as man – early man learned to utilise natural products to his own advantage, and these include wax. Even in ancient stories the use of wax was described, for instance the mythological figure Icarus who used wax as an adhesive to attach his wings, but flew to close to the sun, causing the wax to melt and Icarus to fall into the sea.

The word “wax” was derived from the Anglo-Saxon word weax that meant “that which grows from bees” [Hamilton, 1995]. Materials with similar properties also became known as weax or wachs, and later wax. All the ancient encyclopaedias refer to beeswax only - this wax can be called ancient man’s thermoplastic.

The following definition of wax was formulated by the Deutsche Gesellschaft fur Fettwissenschaft: “Wax is a collective term for a series of natural or synthetic substances that, as a rule, have the following properties: can be solid, pliable to hard, brittle at 20°C, coarse or fine crystalline, translucent to opaque but not glassy, melt above 40°C without decomposition, having a relatively low viscosity just above its melting point, cannot be drawn into threads; consistency and solubility strongly dependent upon temperature; can be polished under slight pressure.” [Hamilton, 1995]. The academic definition of a wax is “an ester of a long-chain aliphatic acid with a long-chain aliphatic alcohol”, but this definition does not include all the other substances present in waxes. Without these other components in waxes, the desired properties will not all be obtained, because the properties depend more on the structure of the wax than on chemical composition.

Despite the widespread use of waxes, very little theory is known about the relationship between the structure and properties of waxes. Material scientists like to have theories
that describe and explain the fundamental data relating properties to structure. Technological advances that will lead to improved or novel formulations will depend on a proper knowledge of the physical chemistry of waxes and the intermolecular forces directing the packing and interaction of long chain molecules in the wax.

Because of the range of substances occurring in waxes, structural analysis to determine structure-property relationships will prove to be difficult. Instead our strategy involves the structural investigation of some of the pure compounds found in waxes. Most waxes consist of either long-chain hydrocarbons, long chain oxygen containing compounds, or mixtures of these. After investigation of the structure of these pure components, binary and tertiary mixtures of these compounds can be investigated, and modifications in the structure induced by mixing can be identified. Structural observations can be used to extrapolate the properties of known mixtures to predict properties of novel mixtures. Simple straight chain compounds with substitution of functional groups will act as templates to determine the change in packing forces induced by different crystallisation conditions, and phase changes occurring on heating and cooling.

A theory on the relationship between the properties and structure of waxes has many practical applications. Prediction of properties on the ground of composition will lead to better utilisation of waxes produced by South Africa’s petrochemical industry. The effect of changing chemical composition, e.g. change in functional end groups or oxidation will be better understood. A theory can produce a framework of reasoning when production problems exist, for example in the crystallisation of waxy substances.

In view of the many uses of waxes, a theory able to describe and explain performance under different environmental conditions will lead to product improvement and customer satisfaction.
4.2 Properties of waxes

The chemical cause of “waxiness” is not well understood – the special character of waxes cannot be fundamentally explained. One parameter that varies among different waxes is the degree of crystallinity. If the components in a wax are of similar chain length, the wax tends to be more crystalline due to ease of crystal growth. However, if the components are different, e.g. branches in chains, rings or difference in functional groups, the crystallisation of the wax will be impaired, resulting in a lower degree of crystallinity. This ability of components to co-crystallise determines the structure, and hence the properties of the wax.

Waxes undergo plastic deformation at temperatures relatively close to room temperature, and most commercial waxes have melting points between 40°C and 120°C. The ability to undergo plastic deformation within a certain temperature range may be attributed to crystallites slipping past each other, facilitated by the presence of smaller particles rolling between bigger ones [le Roux, 1977]. The thin layer of oil covering the crystallites can act as a lubricant in the slipping process.

4.3 Classification of waxes

Various classifications of waxes are found in the literature. Waxes can be classified according to origin, as natural or synthetic, with each group further divided into subgroups. The structures of waxes can also be used for classification for example hydrocarbon waxes are divided into paraffinic and microcrystalline. The categorisation used here will be that of natural and synthetic waxes.
4.4 A few important waxes and uses

4.4.1 Natural waxes

Animal waxes

Beeswax

Beeswax was used as a form of currency in the Middle Ages. This wax is one of the most valuable waxes used today. Beeswax is excreted from wax glands on the abdomen of the bee, and used to build the combs where the honey is stored. The composition of the wax varies with the geographical origin, with the main components being esters with carbon chain lengths ranging from 36 to 54 carbon atoms. A compositional analysis of beeswax is given in Table 4.1.

Brazil and Canada are the main exporters of beeswax. The largest markets are in the manufacturing of candles and cosmetics. The wax is used in smaller quantities in polishes, confections, medicine and art.

Table 4.1: Chemical composition of beeswax [Kirk, 1979].

<table>
<thead>
<tr>
<th>Component</th>
<th>Formula</th>
<th>% wt</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Esters</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>myricyl palmitate</td>
<td>C_{15}H_{31}COOC_{30}H_{61}</td>
<td>23.0</td>
</tr>
<tr>
<td>lacceryl palmitate</td>
<td>C_{15}H_{31}COOC_{32}H_{65}</td>
<td>2.0</td>
</tr>
<tr>
<td>myricyl cerotate</td>
<td>C_{25}H_{51}COOC_{30}H_{61}</td>
<td>12.0</td>
</tr>
<tr>
<td>myricyl hypogaete</td>
<td>C_{13}H_{27}CH=CHCOOC_{30}H_{61}</td>
<td>12.0</td>
</tr>
<tr>
<td>ceryl 2-hydroxypalmitate</td>
<td>C_{14}H_{29}(OH)COOC_{26}H_{51}</td>
<td>8.0 - 9.0</td>
</tr>
<tr>
<td>acid esters</td>
<td></td>
<td>4.0 - 4.5</td>
</tr>
<tr>
<td>diesters</td>
<td></td>
<td>6.0 - 6.5</td>
</tr>
<tr>
<td>acid diesters, triesters</td>
<td></td>
<td>3.0 - 3.5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td>70.0 - 71.5</td>
</tr>
<tr>
<td>cholesterol esters of fatty acids</td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>coloring agent</td>
<td></td>
<td>0.3</td>
</tr>
<tr>
<td>lactone</td>
<td></td>
<td>0.6</td>
</tr>
<tr>
<td>free alcohols: C_{34} - C_{36}</td>
<td></td>
<td>1.0 - 1.25</td>
</tr>
<tr>
<td><strong>Free wax acids</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>lignoceric acid</td>
<td>C_{23}H_{47}COOH</td>
<td>1.0 - 1.5</td>
</tr>
<tr>
<td>cerotic acid</td>
<td>C_{26}H_{51}COOH</td>
<td>3.8 - 4.4</td>
</tr>
<tr>
<td>melissic acid</td>
<td>C_{24}H_{59}COOH</td>
<td>2.0</td>
</tr>
<tr>
<td>psyllic acid</td>
<td>C_{31}H_{63}COOH</td>
<td>1.3 - 1.5</td>
</tr>
<tr>
<td>hypogaeic acid</td>
<td>C_{13}H_{27}CH=CHCOOH</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td>9.6 - 10.9</td>
</tr>
<tr>
<td><strong>Hydrocarbons</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pentacosane</td>
<td>C_{25}H_{52}</td>
<td>0.3</td>
</tr>
<tr>
<td>heptacosane</td>
<td>C_{27}H_{56}</td>
<td>0.3</td>
</tr>
<tr>
<td>nonacosane</td>
<td>C_{29}H_{60}</td>
<td>1.0 - 3.0</td>
</tr>
<tr>
<td>hentriaicosane</td>
<td>C_{31}H_{68}7</td>
<td>8.0 - 9.0</td>
</tr>
<tr>
<td>melene</td>
<td>C_{28}H_{57}CH=CH_{2}</td>
<td>2.5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td>12.1 - 15.1</td>
</tr>
</tbody>
</table>
Other animal waxes include wool grease and lanolin from the hair of sheep, and spermaceti wax from the sperm whale, but trading of spermaceti has been banned due to pressure from environmentalists.

**Vegetable waxes**

**Carnauba wax**

Carnauba wax is obtained from the palm tree, *Copernicia prunicia* that grows exclusively in Brazil, with the Brazil government controlling the marketing. The wax is mechanically removed from the dried fronds of the palm. The wax is harvested twice a year. Carnauba wax is a very hard wax with the highest melting point (82° C – 86° C) of naturally occurring waxes. It polishes to a high gloss, making it a component of almost all polishes. Carnauba wax is often used in admixture with other waxes to improve their properties, e.g. it reduces the tendency to crystallise out [Hamilton, 1997].

<table>
<thead>
<tr>
<th>Component</th>
<th>% wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatic esters</td>
<td>40.0</td>
</tr>
<tr>
<td>ω-hydroxy esters</td>
<td>13.0</td>
</tr>
<tr>
<td>cinnamic aliphatic diesters</td>
<td>8.0</td>
</tr>
<tr>
<td>Free fatty acids</td>
<td>3.0 - 3.5</td>
</tr>
<tr>
<td>Alcohols</td>
<td>2.0 - 3.0</td>
</tr>
<tr>
<td>Lactides</td>
<td>2.0 - 3.0</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>1.5 - 3.0</td>
</tr>
<tr>
<td>Resins</td>
<td>4.0 - 6.0</td>
</tr>
<tr>
<td>Moisture and inorganic residue</td>
<td>0.5 - 1.0</td>
</tr>
</tbody>
</table>

*Table 4.2: Composition of Carnauba wax [Kirk, 1979].*
Carnauba wax is used in cosmetics for example lipstick, to give additional strength, as glaze in the food industry and as paper coatings. It is used in lubricants, controlled release matrix for fertilisers and insecticides, and in candies and gums. In many products cheaper synthetic waxes have replaced Carnauba wax.

Other plant waxes include Japan wax, Ouricury wax, Douglas Fir bark wax, rice-bran wax, candelilla wax and jojoba wax. Their properties and uses have been described extensively [Hamilton, 1997].

Mineral waxes

These waxes are derived from naturally occurring deposits, and include Montan wax from coal, peat waxes, and Ozokerite.

Petroleum waxes

Petroleum waxes are hydrocarbons of the following types: paraffin, semi-microcrystalline and microcrystalline.

These waxes are obtained from petroleum by various techniques:

i) dewaxing of petroleum products
ii) fractional crystallisation of slack waxes
iii) purification of crude paraffin waxes
iv) addition of additives to paraffin waxes

A paraffin wax consists mainly of normal alkanes. Semi-microcrystalline and microcrystalline waxes do not only contain straight chain hydrocarbons, but also isoalkanes and cycloalkanes.

Paraffin waxes are used in products to increase water resistance. Applications include packaging like cups and containers, and in candles.
4.4.2 Synthetic waxes

**Fischer-Tropsch waxes**

Fischer-Tropsch waxes are of major importance in the South African chemical industry and are produced by SASOL (South African Coal, Oil and Gas Corporation Ltd) at Sasolburg. The Fischer-Tropsch process involves the polymerisation of carbon monoxide over iron catalysts at high pressures to produce hydrocarbons. The paraffin wax is obtained by reducing the temperature, and consists mainly of $C_{17}H_{36}$ to $C_{25}H_{52}$ n-alkanes [Hamilton, 1997]. The composition of Fischer-Tropsch waxes is unique in that the majority of alkanes produced is unbranched. Fischer-Tropsch waxes are white, hard and glossy. These waxes are added to petroleum paraffin waxes to increase the hardness and melting point. SASOL has the capacity to annually produce 27 000 tons of hard and 11 000 tons of soft wax.

Other synthetic waxes produced include carbowaxes (solid polyethylene glycols), synthetic esters (e.g. hexadecyl octadecanoate) and polyethylenes catalytically obtained from ethylene.

4.5 Use of waxes

Gaius Plinius Secundus (23-79 AD) wrote in his encyclopaedia on nature that there were a thousand uses for wax in everyday life [Le Roux, 1977]. Clearly it would be impossible name every modern use of wax, but a few of the most important uses are briefly discussed here.

One of the oldest uses of wax, beeswax is particular, was in the making of candles. Nowadays most candles are manufactured from mixtures of paraffin waxes and stearic acid. Hard waxes like Carnauba, Montan and additives like stearic acid and palmitic acid improve the dripping properties of candles.
Paraffin waxes are used in electrical insulation, firstly as coating for the wire as insulation, secondly to add moisture resistance, and thirdly as a sealant.

In the food industry waxes are used in both the products and the packaging. Paper products impregnated with wax are used for packing of food products. Fruit and vegetables are coated with wax to retard moisture loss and provide lustre and shine. Wax is used as a coating for cheese to inhibit the growth of fungus and keep in moisture.

Most cosmetic creams have a wax foundation. Waxes are added to other cosmetic products like pencils and lipsticks to improve the hardness.

Waxes are components of polishes for floors, automobiles, shoes and furniture. Polish must prevent water, vapour and air penetrating the surface it is applied to. Beeswax increases the flexibility of the coating, and Carnauba and Montan wax add gloss and hardness to a polish. The right consistency of the polish can be obtained by addition of the softer paraffin waxes.

4.6 Structure of waxes

Because waxes are complex mixtures of long chain organic compounds including alkanes, fatty acids, alcohols, aldehydes, ketones and esters, structural investigations can be difficult. Can a representative single crystal of a wax really be obtained? An important fact to keep in mind is that it is not the absolute chemical composition of a wax that lends it its properties, but rather the molecular structure.

The primary alcohols, acids and esters found in naturally occurring waxes have an even number of carbon atoms in the straight chain (except for a very small percentage that may be odd.). Ketones and hydrocarbons mainly have an odd number of carbon atoms in the chain (see table 4.1 - Composition of beeswax). Most components in waxes are straight chains, except for Carnauba wax that contains a percentage of methoxycinnamic acids and -esters.
4.6.1 Synthetic waxes

**Fischer-Tropsch and derived waxes**

An extensive research programme on waxes was initiated at Sasol in the 1960’s, with research focussed mainly on Fisher-Tropsch (F-T) and F-T derived waxes [le Roux, 1977]. The products of the Fischer-Tropsch process are mixtures of normal and branched alkanes and alkenes [Lourens and Reynhardt, 1979]. A new classification of waxes according to the degree of crystallinity of the wax was proposed by Sasol’s research group. Two extreme types of waxes, type I, a highly crystalline wax, and type II containing amorphous material, were defined. Most waxes lie somewhere between types I and II, depending on the degree of crystallinity. Evidence was given that a type I wax consists of plate-like crystallites. In these plates regions of disorder (called defects) are found.

The plasticity of a type I wax is due to the following:

i) molecules moving within the crystallites

ii) crystals cleaving through defects

iii) slipping of crystallites over each other, facilitated by the presence of smaller crystallites rolling between bigger ones.

iv) lubrication provided by a layer of oil and molten wax covering the crystallites and holding them together

Waxes of type I crystallise easily, due to the fact that their molecules do not differ much in chain length and functional groups. This makes it possible to obtain a single crystal of a type I wax.

Type II waxes can be described as crystallites contained in a viscous, amorphous matrix. Differences between molecules inhibit crystal growth. Plastic deformation is attributed to the viscous flow of the matrix and bending of the thin crystallites.
Intermediate waxes are structural hybrids between the extreme type I and II waxes. Based on this range of possible waxes between type I and type II waxes, four models for paraffinic waxes were proposed.

These models for waxes are applicable to both Fischer-Tropsch paraffinic wax, and the derived oxidised wax. The structure of the paraffinic waxes is more crystalline, and the oxidised waxes contain more amorphous regions where hydrogen bonding is important.

**Paraffinic Fischer-Tropsch Waxes**

Mixtures of n-alkanes act as models for paraffinic waxes. However, because waxes contain various impurities, the results obtained for n-alkanes cannot be applied directly to the structures of paraffinic waxes.

The ability of molecules with different chain lengths to co-crystallise is attributed to the lateral movement of shorter molecules within the lamella. This movement then compensates for the differences in chain lengths among the molecules. Conformational disorder near the lamellar surface due to kinks in chains also acts to reduce the difference in chain lengths between molecules. The lamellar surface, must however, still be even enough to nucleate the next layer [Dorset, 1995].

Single crystals of a paraffinic wax were grown by Stockhuizen and Pistorius [1970]. The crystal consisted of n-alkanes from \( C_{28} \) to \( C_{34} \). The unit cell dimensions were \( a=5.00 \) Å; \( b=7.50 \) Å, \( c=85.0 \) Å with space group \( Pbnm \).

Based on the range of possible waxes between type I and type II waxes, four models for paraffinic waxes were proposed [le Roux and Loubser, 1980]. In Model I bundles of extended chains are contained in an amorphous matrix. Model II contains bundles that have grown in size to form thin plates. Model III contains thicker plates (crystallites) and liquid trapped in the voids between the crystallites. In this model the amorphous matrix is
not required. Model IV consists of a conglomerate of plates with extended chains, with the chain ends not aligned.

Fig 4.1: Possible structures of paraffinic waxes

Investigations indicated that model III is the best model to describe the structure of paraffinic waxes [le Roux and Loubser, 1980]. A structure was proposed for model III paraffinic Fischer-Tropsch waxes by le Roux et al [1976] (See Fig 4.2). The wax contains regions that differ in the degree of crystallinity. An amorphous phase A is formed by the ends of chains of different lengths. A rigid amorphous phase B is the result of branches in some molecules. A mobile amorphous region C, consists of low melting iso-alkanes. The largest percentage of the wax (region D) resembles the pure n-alkane C_{28}H_{58}. This highly crystalline region has an orthorhombic structure at room temperature, and transforms to a hexagonal modification just below the melting point of the wax [Basson and Reynhardt, 1992].
An X-ray diffraction investigation was conducted by Retief and le Roux [1983] to gain insight on the structure and crystallinity of paraffinic F-T waxes. The structural model was based on the proposed type I and II waxes. From NMR investigations it was found that a high percentage of liquid is still present in the wax within a range of temperatures below the solidification point of the wax. This indicates the presence of liquid in the voids between crystallites. On further cooling, crystallisation within the liquid in the voids commences. Smaller crystallites will be trapped between the larger crystallites, with liquid still present in the voids. The process is repeated, resulting in a range of crystallite sizes. The proposed model for structure of paraffinic F-T waxes consists of thick crystallite plates with oil trapped in the voids between the crystallites. Cohesion among crystallites is enhanced by the oil in the voids, and at higher temperatures, the molten wax in the voids. The plasticity of the wax is a result of the sliding of one crystallite over another, helped by smaller crystallites, and the presence of liquid in the voids.

This model is not only applicable to F-T paraffinic wax, but also to other paraffinic waxes. Thus, paraffinic wax can be described as a type I wax, with a high degree of crystallinity due to similarities between the alkane components.

The dependence of unit cell dimensions of F-T paraffinic hard wax on temperature was indicated by Reynhardt [1986]. Prominent peaks on the powder diffraction pattern of hard wax are the 110 and 020 peaks in the range $20^\circ<\theta<25^\circ$. These reflections, together with the 200 reflections were used to determine the dependence of $a$ and $b$ on temperature. In the low temperature, orthorhombic modification, the $a$ unit cell parameter is a linear function of temperature. In the high temperature, hexagonal phase the change in $a$ with temperature is smaller than in the low temperature phase. The $b$ unit cell dimension is
also linearly dependent on the temperature, with a smaller increase with temperature in
the low temperature phase than in the high temperature phase. The $c$ unit cell dimension
is independent of temperature, and stays nearly constant at $143 \pm 0.5 \text{ Å}$.

It was found that structural changes take place in F-T paraffinic wax with time. These
changes were, however, only observed in samples where processes such as melting or
mechanical grinding have disturbed the crystallites. Retief and le Roux [1983] proposed
that the rate of solidification of the wax from the melt is too high to cause ordering
among molecules to form different stable solid solutions. The movement of molecules
from highly disordered zones to regions with similar chain length is predicted. This result
in a more ordered, stable structure. This process can be associated with the secondary
crystallisation in paraffinic F-T waxes. Changes observed visually in samples of F-T
paraffinic waxes can be explained by the migration of molecules form an unstable
location to a more stable arrangement in the crystal. This observation indicates that waxes
are not rigid, inert materials, but undergo changes that can influence the physical
properties and, in turn, the performance of wax products.

**Oxidised Fischer-Tropsch waxes**

At Sasol, oxygen is bubbled through a portion of the paraffinic F-T wax, resulting in
catalytic oxidation of the alkanes. The oxidised wax exhibits better emulsifiability, better
retention of solvent and higher gloss and mechanical hardness [le Roux, 1979, Brett et al,
1990].

In oxidised F-T wax, a variety of compounds are found due to the random attack of
oxygen. Even though hydrogen bonding will promote the crystallisation of these
compounds, the difference in functionality between compounds will hamper
crystallisation. This results in a relatively disordered structure for oxidised F-T wax. A
structural model for this wax was proposed by le Roux [1979] from results obtained by
X-ray diffraction, IR spectroscopy and NMR measurements. Above the solidification
point, moieties such as alcohol dimers, trimers and molecules bonded to more than one
site are expected to be present. On freezing the alkanes and unbonded oxygen containing compounds will crystallise. Solid solutions may be formed between fatty acids and other components.

The crystallisation of components in lamella, with alkyl parts parallel, may be impeded by the formation of hydrogen bonds between functional groups. This will cause extension of chains beyond the lamellar interface, resulting in a mobile phase. The author suggested that certain zones in the wax are crystalline, containing crystallites of a compound, or a solid solution if the chain lengths allow it. In Fig 4.3 this proposed structure is shown graphically. Note the association of the oxygen containing functional groups.

Fig. 4.3: Proposed structure of oxidised F-T wax.

4.6.2 Natural waxes

Paraffinic waxes

Petroleum waxes consist of saturated hydrocarbons, mainly \( n \)-alkanes with chain lengths ranging from \( C_{18} \) to \( C_{65} \). These waxes usually have a Gaussian distribution of components.

Structural investigations on commercial multi-component paraffin waxes and petroleum solid deposits were conducted by Dirand et al [1998]. It was indicated that a paraffin wax containing a continuous distribution of consecutive \( n \)-alkanes crystallises in a solid solution. This solid solution is orthorhombic with the molecules packing in lamella, similar to what is found for pure \( n \)-alkanes and binary mixtures.
The orthorhombic structure resembles a pure \( n \)-alkane with chain length equal to the average chain length of the components in the wax. The \( c \) unit cell dimensions is a linear function of this average hydrocarbon chain length. The proposed packing of \( n \)-alkanes of different chain lengths is indicated in Fig 4.4 – molecules with chain lengths longer than that of the average chain length fold to be accommodated in the lamella.

Fig 4.4: Proposed packing of \( n \)-alkane molecules with different lengths in paraffinic waxes

Dorset [1995] investigated the structures of model waxes. An equimolar mixture of even \( n \)-alkanes \( \text{C}_{26} \) to \( \text{C}_{36} \) was seen as representative of a paraffin wax. Electron diffraction was utilised to investigate the structure of epitaxially orientated samples of the mixture. Regions with structures similar to the pure \( n \)-alkanes \( \text{C}_{32}\text{H}_{66} \) and \( \text{C}_{33}\text{H}_{68} \) were identified. The co-crystallisation of components with different chain lengths is facilitated by the longitudinal movement of the shorter components. This movement was indicated by atomic occupancies smaller than unity. The atomic occupancies towards the ends of the molecules decrease, with the occupancy of the molecule exhibiting an approximately Gaussian fall-off.

The structure of petroleum wax from a paraffin candle resembles the structure of pure \( n \)-\( \text{C}_{29}\text{H}_{60} \) [Dorset, 1995]. The packing exhibits orthorhombic symmetry with possible space groups \( \text{A2}_\text{jam} \) or \( \text{Aa} \). The experimentally obtained unit cell dimensions were \( a = 7.42 \, \text{Å} \), \( b = 4.96 \, \text{Å} \), \( c = 76.58 \, \text{Å} \). The structure was derived from the known structure of \( n \)-\( \text{C}_{29}\text{H}_{60} \). Atomic occupancies were determined, indicating the co-crystallisation of \( n \)-alkanes with different chain lengths.
Plant and insect waxes

Dorset [1999a] investigated the structures of various naturally occurring waxes by means of electron diffraction, and compared the results with the structures of the more ordered paraffin derived waxes. The main difference between natural waxes and F-T waxes is the occurrence of branched moieties in natural waxes [Basson and Reynhardt, 1988c].

Beeswax

This natural wax generally do not exhibit a lamellar structure – instead a nematic structure with parallel chains but little or no separation into layers is exhibited [Dorset, 1997a, 1999a]. Contrary to the petroleum derived waxes having relatively few components and crystallising in layers, beeswax has a much more complex composition. In this naturally occurring wax, the very long chain ester molecules present may act as 'bridging molecules being part of more than one layer. If many of these bridging molecules are present, the electron diffraction pattern will resemble that of polyethylene with folded chains.

Dorset [1999a] provided evidence of improvement of the ordering of these naturally occurring waxes by use of a nucleating substrate. Beeswax (composition: tetradecyl hexadecanoate (myricyl palmitate) - 72%; free acids - 13%; hydrocarbons - 12%) was crystallized epitaxially by use of benzoic acid to direct the chain axes parallel to the substrate. The lamellar spacing was found to be $66.55 \pm 1.35 \text{ Å}$. This results agrees well with the expected spacing of the orthorhombic form of myricyl palmitate, of 62.8 Å calculated as described by Nyburg and Potworowski [1973]. The Gaussian decrease of the lamellar intensities is a clear indication of the lamellar structure.

Studies by X-ray diffraction [Basson and Reynhardt, 1988a] indicated that the powder diffraction pattern of beeswax resembles that of oxidised Fischer-Tropsch medium wax. This indicates orthorhombic packing of the molecules with the chains perpendicular to the lamellar surface.
An electron diffraction study was conducted on microcrystals of beeswax [Dorset, 1995]. The diffraction pattern resembles the pattern of multi-components paraffin waxes also indicating an orthorhombic solid solution. There is no transformation to a rotator phase before melting, behaviour characteristic of even n-alkanes containing more than 38 carbon atoms.

Dorset [1995] combined long chain esters to model beeswax. The melting point compared well to that of natural beeswax. The structure resembled that of orthorhombic n-alkanes $\text{C}_{40}\text{H}_{82}$, $\text{C}_{41}\text{H}_{84}$ or $\text{C}_{42}\text{H}_{86}$. The space group of the even n-alkanes was found to be $Pca2_1$ and $A2_1am$ (or $Aa$) for the odd. The structural resemblance between the beeswax model and natural beeswax was, however, not satisfactory, as the average lamellar layers were much thinner than those found for natural beeswax.

**Montan wax**

Montan wax is fossilised plant wax with long chain esters as the main components. The composition of Montan wax is: long chain esters ($\text{C}_{24} - \text{C}_{30}$), long chain acids, (22–26%), long chain alcohols, ketones and alkanes (7–15%) and resins [Basson and Reynhardt, 1988c]. This wax posseses a high degree of crystallinity [Dorset, 1997a], with very little branching. The lamella pack in the orthorhombic modification, with a structure resembling that of $\text{C}_{29}$ or $\text{C}_{30}$. This high crystallinity indicates the similarity in functional groups and chain length of the constituents of the wax.

**Plant waxes**

**Carnauba wax**

The main components of Carnauba wax are long chain esters. The composition of the wax is: hydrocarbons (2%), aliphatic and aromatic esters (84%), fatty acids (3%), long chain alcohols (3%), with the rest being comprised of lactides, resins, moisture and inorganic matter [Basson and Reynhardt, 1988b]. It was reported [Basson and Reynhardt, 1988b].
1988b] that Carnauba wax crystallises in an orthorhombic modification. DSC measurements indicate that the wax undergoes a solid-solid transformation before melting. In plant waxes, long molecules act as bridges between crystalline regions. Ordered Carnauba wax samples were prepared by heating the wax in the presence of a nucleating substance [Dorset, 1999a]. In previous electron diffraction studies [Dorset, 1997a], no clear lamellar repeat was observed for this wax - the diffraction pattern resembled that of polyethylene. Electron diffraction results of the epitaxially orientated wax, however, showed three lamellar orders with a lamellar spacing of \(42.32 \pm 1.57 \text{ Å}\).

**Other plant waxes**

It was found [Reynhardt and Riederer, 1991; Reynhardt and Riederer, 1994; Reynhardt, 1997] that plant waxes possess a low degree of crystallinity. The wax obtained from the leaves of *Citrus aurantium* L. was approximately 80% amorphous, with the crystalline regions formed mainly by alcohols and long-chain esters [Reynhardt and Riederer, 1991]. The cuticular wax of *Hordeum vulgare* L. contains amorphous and crystalline regions [Reynhardt, 1997]. The crystalline zones have a bilayered structure. Hydrogen bonding prevents the formation of a more crystalline wax by means of phase separation, but leads to a very high melting point. As expected, the degree of crystallinity is very low.

**4.7 Conclusion**

The blending of different waxes and of waxes with additives is done mainly by means of empirical experiments. It is, however, necessary to understand the fundamental variables influencing the structure and properties of waxes. By understanding the structure property relationships of naturally occurring waxes, it will be possible to produce waxes with similar properties synthetically, resulting in economical profits.

Knowledge of the structural aspects of waxes will not only explain the properties of the waxes, but will lead to the development of novel formulations with desired properties.
Chapter 5

*n-Alkanes*

*n-Alkanes* are a logical starting point for understanding the phase transitions and crystallography of long chain molecules. The structural and thermal behavior of functionalized hydrocarbon systems is analogous to those of pure *n*-alkanes. These simple chains form part of many molecules in organic, polymeric and biological systems, including liquid crystals, surfactants and lipids [Sirota, 1992]. Hydrocarbon chain systems can act as models for synthetic polymers and lipid biomembranes. A better understanding of *n*-alkane phase behavior will aid in understanding many other systems.

Because no experimental structural investigation of *n*-alkanes was performed in this investigation, only an introduction and selected examples from the literature will be presented. The structure and thermal behavior of *n*-alkanes are good reference points to compare the behavior of other functionalized hydrocarbons with.

An important factor influencing the structure and properties of *n*-alkanes is the parity of the number of carbon atoms in the chain. This is often referred to as the "odd-even" effect. It is generally found that the even *n*-alkanes are more stable than the odd ones. Gerson *et al* [1993] investigated the saturation temperatures for the *n*-alkane series \( C_{18}H_{38} \) to \( C_{29}H_{60} \). The odd *n*-alkanes were found to have consistently lower saturation temperatures than those of the even *n*-alkanes indicating lower stability by dissolving at lower temperatures.

Polymorphism is exhibited by certain long *n*-alkanes. The specific polymorph formed depends on the temperature, solvent system, and impurities present. Meltgrown samples tend to show more complex structures than solution grown samples, sometimes forming metastable phases that change with time.

In this section \( C_n \) represents a normal alkane with \( n \) carbon atoms in the molecule.
5.1 Crystal Structure

Four crystalline modifications are exhibited by \( n \)-alkanes: triclinic, monoclinic, orthorhombic and hexagonal, depending on the temperature, number of carbon atoms, parity of the carbon atoms and the purity. At ambient conditions normal \( n \)-alkanes crystallize in three different polymorphic forms: [Heyding, 1990]. For \( n \) even, \( 6 < n < 26 \) the structure is triclinic, spacegroup \( P1 \); for \( n \) even, \( 26 < n < 36 \) it is monoclinic, spacegroup \( P2_1/a \), for \( n = 26 \) both the triclinic and monoclinic modifications are observed. For \( n \) odd, \( 11 < n < 19 \) the structure is orthorhombic, \( Pcbm \), if \( n \) is the number of carbon atoms in the chain. The specific polymorphic modification is, however, also dependent on the thermal history of the sample, and its purity.

\( n \)-Alkanes crystallize in lamellae (layers), with the terminal methyl groups forming the surface of the lamellae. The contact plane between the layers is the (001) plane. In the lowest temperature modification the molecules are in the trans (extended) conformation and parallel to one another. In order to accommodate the long molecule, one of the axes of the unit cell (by convention the \( c \) axis) is very long. For each of the above-mentioned polymorphic forms, the long spacings \( d(001) \) change smoothly with \( n \) (the number of carbon atoms in the chain). This indicates isostructurality in the series. Chains start to fold only if there are a hundred and fifty or more carbon atoms in the chain [Peterson, 1985].

If the overall symmetry is orthorhombic, the long chain axes are perpendicular to the surface of the lamellae and the orthorhombic sub-lattice contains four methylene (CH\(_2\)) groups. If the chains are tilted relative to the lamella, monoclinic or triclinic symmetry results with the monoclinic sub-lattice containing four methylene groups. The triclinic sub-lattice contains one methylene group. If consecutive lamella are related by a 180° rotation, the symmetry is pseudo orthorhombic.

Even numbered \( n \)-alkanes may crystallize in the orthorhombic modification rather than the expected monoclinic or triclinic modifications, if neighboring homologues are present as impurities [Hemmami, 1995]. The formation of orthorhombic modifications is characteristic behavior for solid solutions of long chain molecules.
As the number of carbon atoms in the paraffin chain increases, the energy difference between the monoclinic and orthorhombic modifications decreases. Even though the monoclinic modification is a lower energy state than the orthorhombic, the energy difference between these two forms becomes too small to be a significant driving force to cause a transition.

Nyburg and Powotowski [1972] predicted structures and cell dimensions of \( n \)-alkanes in an isostructural series by extrapolating the structures of known "key" \( n \)-alkanes. This prediction of unit cell dimensions and structure is based on the assumption that the carbon chain preserves its orientation with respect to the crystallographic axes, and that the chain is in the \textit{trans} configuration. The following "key" structures were extrapolated:

1. \( \text{C}_{23} \ Pcbm \) - orthorhombic structure of odd-numbered \( n \)-alkanes
2. \( \text{C}_{18} \ P1 \) - triclinic structure of even-numbered \( n \)-alkanes, \( (6<n<36) \) [Nyburg and Luth, 1972]
3. \( \text{C}_{36} \ P2_{1}/a \) - monoclinic structure of even-numbered \( n \)-alkanes, \( (26<n<38) \) [Shearer and Vand, 1956]
4. \( \text{C}_{36} \ Pca2_1 \) - orthorhombic structure for the even-numbered \( n \)-alkanes \( (n>36) \) [Teare, 1959]

Nyburg and Pickard [1976] used this method to predict the cell dimensions and atomic coordinates for the series \( \text{C}_n\text{H}_{2n+2} \), \( n \) even, \( n=10, 12, 14 \) and 16. These values were compared to values obtained experimentally by powder photographs. It was found that the agreement for \( n=12 \) and \( n=14 \) is good, but less good for \( n=10 \) and \( n=16 \).

Dirand \textit{et al} [1999] determined the relationship between the \( c \) unit cell dimension and the number of carbon atoms in the chain for the different structural modifications. For the orthorhombic phase the following linear equation was determined:

\[
c(\text{Å}) = 1.2724n + 1.8752.
\]

The \( d(002) \) value corresponds to the sum of the chain length and the gap between the lamellar planes. The slope represents the increase in chain length per carbon atom. The gap between the layers was found to be 3.1476 Å, and the length of a carbon chain 1.2724\((n-1)\) Å. In the triclinic and monoclinic modifications the long spacing has a lower value due to the tilt of the molecules relative to the lamellar plane. In these modifications the \( c \)-axis is inclined to the normal lamellar surface, but not parallel.
to the \( n \)-alkane chain axis. From literature values it was determined that the average gap between monoclinic layers is 2.98 Å, and for triclinic layers 2.74 Å.

5.2 Polytypism in \( n \)-alkanes

Polytypic structures of \( n \)-C\(_{28}\)H\(_{58}\) and \( n \)-C\(_{36}\)H\(_{74}\) were investigated by Boistelle et al [1976]. The authors provided evidence that the structure consists of stacking of alternate monoclinic layers. The layers are related to one another by a twofold axis normal to the (001) plane. The overall symmetry was found to be pseudo-orthorhombic, with space group \( Pbca \). It was indicated [Boistelle and Aquilano, 1977] by calculations performed with a Lennard-Jones 6-12 potential function that the formation of the polytype is possible from both an energetic and a structural point of view.

Rinaudo et al [1979] observed that crystals of \( n \)-C\(_{34}\)H\(_{70}\) also exhibited coalescence between the monoclinic and orthorhombic polymorphs of the \( n \)-alkane. From the growth spirals on the (001) common faces of the aggregates, it was proved that the structure consists of vertical orthorhombic chains stacked on the tilted monoclinic chains. The layers are rotated with respect to each other around an axis normal to the (001) plane. The crystals did not exhibit the normal lozenge shaped monoclinic morphology, but were elongated.

5.3 Thermal behavior

Various studies have indicated that \( n \)-alkanes exhibit complex phase transitions just below the melting point [Snyder et al, 1981; Maroncelli et al, 1982; Ungar, 1983]. The ordered, stable modification transforms to a disordered phase at higher temperatures. All even numbered \( n \)-alkanes, \( n > 22 \) exhibit a phase transformation before melting. Odd \( n \)-alkanes from \( C_9 \) to \( C_{45} \) undergo at least one solid-solid phase transition, and some of the longer members show up to four high-temperature solid phases in addition to the low temperature phase. The thermal behavior of several odd \( n \)-alkanes and binary mixtures was reported in the literature [Snyder et al, 1981; Ungar, 1983].

In the high temperature phases, \( n \)-alkane chains have rotational freedom they do not posses at lower temperatures, and kinks are formed in the chains. These phases are called
the rotator phases and are indicated by R. If more than one rotator phase is present, a subscript indicates the number of the rotator phase with R₁ being the rotator phase occurring at the lowest temperature. Phase transitions of one rotator phase to another are manifested as minor peaks in DSC tracings, and are only visible if highly sensitive instruments are used. These transitions are often irreversible and kinetically very slow.

In the rotator phase, disorder is present in the form of conformational defects and rigid body longitudinal movements of molecules. Disorder can be described as any deviation from the regular, all-trans arrangement of chains found in the low-temperature structure.

Three conformational defects have been identified: “end gauche”, “kink” and “double gauche” [Maroncelli et al, 1982; Snyder et al, 1981]. Of these, the most common are kinks. The concentration of these defects is a linear function of temperature and chain length, with increasing concentration with increasing n and temperature. Correlations among the different types of disorders have been proved to exist.

Fig 5.1: Conformations of n-alkanes: (a) All-trans (b) End gauche (c) Double gauche (d) Kink

Four crystallographic types of rotator phases have been found [Craevich, 1984]. For even n-alkanes, n ≤ 26 the rotator phase is hexagonal. Odd numbered n-alkanes, 11 ≤ n ≤ 21, shows a R₁ phase with an orthorhombic packing of molecules, and n=23 and n=25 exhibits both the R₁ and R₁₁ rotator phases. For n-alkanes with n > 26 a R₁₁ (triclinic) or R₁₄ (monoclinic), or both R₁₁ (lower temperature) and R₁₄ (higher temperature) is exhibited.
In the first rotator phase, $R_1$ ($Fmmm$) the chains are packed in an orthorhombic face centered fashion. Spectroscopic measurements have shown that there are short-range correlated rotational motions. The $R_1$ rotator phase is the most abundant high temperature phase and is found in odd-numbered $n$-alkanes from $C_{11}$ to $C_{25}$ and in mixed crystals of both even and odd $n$-alkanes in this range of chain lengths.

In the second rotator phase, $R_{II}$ ($R3m$) the chains are in a hexagonal modification, rotating about their long axes with no correlation in the rotation. The chain axis is normal to the lamellar surface. In this modification the molecules posses long-range order, making $R_{II}$ a crystalline phase. The $R_{III}$ rotator phase exhibit triclinic symmetry, and the $R_{IV}$ and $R_{V}$ are high temperature monoclinic modifications [Sirota et al., 1992; Ungar, 1983]. In the rotator phase all molecular sites in the unit cell are crystallographically equivalent, a result of the averaging of several molecular orientations in the direction of the long axis [Ungar and Masic, 1985]. As the chain length increases, conformational disorder in the rotator phases increases.

The disorder in the $n$-alkanes $C_{23}$ and $C_{25}$ was investigated by X-ray diffraction [Craevich, 1985]. These two odd $n$-alkanes exhibit two rotator phases with increasing temperature. The first rotator phase, rotator I ($R_I$), is quasi-hexagonal, and the second, rotator II is hexagonal. For the odd $n$-alkane $C_{21}$ only one rotator phase, $R_I$ was observed [Denicolo et al., 1981].

Basson and Reynhardt [1990] identified a defect chain motion in $n$-alkanes by means of nuclear magnetic spin-lattice relaxation time measurements. These motions were observed in the rotator phase. The highest concentration of these defects was at the ends of the chains, and was found to decrease exponentially to the middle of the chain. It was estimated that the energy difference between the all-trans conformation and the defect conformation is approximately 10 to 14 kJ/mol.

The odd-even effect is also exemplified in the rotator phases. Even in the high temperature modification, the molecules retain certain characteristics associated with their parity [Craevich et al., 1985]. The stacking of lamella differs in the rotator phases of even and odd $n$-alkanes. The authors demonstrated the existence of defects in the form of kinks in odd $n$-alkanes, $C_{19} - C_{27}$, but could not find evidence for these kinks in the even
$n$-alkanes, $C_{22} - C_{28}$. This indicates stability possessed by even $n$-alkanes against the formation of kinks.

Toda et al [1991] employed optical microscopy to investigate the lateral crystal habits of $n$-alkanes just below melting point. It was found that the morphology of the crystal is dependent on the polymorphic phase. $n$-Alkanes crystallized from the solution at ambient conditions is well faceted and diamond shaped. The crystals changed to circular in the rotator phase. The authors speculated that thermal roughening due to phase transitions causes the rounding of lateral habits of the crystal.

5.4 Structure determinations

5.4.1 Even $n$-alkanes

Reynhardt et al [1994] compared the structures of solution-grown and melt-grown samples of $n$-hexatriacontane ($n$-$C_{36}H_{74}$). Four polymorphs have been reported for this compound [Fenrych et al, 1996]: two orthorhombic [Teare, 1959] and two monoclinic modifications [Shearer and Vand, 1956]. The monoclinic modifications can be obtained from the orthorhombic by shifting of the chains parallel to the $c$-axis. Solution-grown samples exhibited an orthorhombic structure, while melt-grown samples were found to be a mixture of a monoclinic and two orthorhombic structures. Shearer and Vand [1956] determined the structure of the monoclinic form by rotation-, oscillation- and Weissenberg photographs.

The structure of $n$-tetracosane ($n$-$C_{34}H_{70}$) [Nyburg & Gerson, 1992] was determined from a twinned crystal by applying overlap corrections. $n$-Alkane crystals are especially prone to twinning, a phenomena that may be related to the formation of the polytypic structures discussed previously.

It was found [Fenrych et al, 1997] that $n$-$C_{46}H_{94}$ ($n$-hexatetracontane) exhibited no solid-solid phase transition before melting, but powder diffractograms measured at increasing temperatures showed a clear temperature dependence of the $a$ and $b$ dimensions of the unit cell, as well as the lamellar spacing. The $b$ cell dimension was found to increase.
with increasing temperatures, and the \( \beta \) angle increased progressively from 100° at 335K to 104.5° at 346K. This is probably due to a gradual transition from the orthorhombic structure to the monoclinic structure by shifting of the molecules along the \( c \) axis. From solution the orthorhombic structure is formed, but a mixture of the orthorhombic and monoclinic structure is formed from the melt.

### 5.4.2 Odd \( n \)-alkanes

Odd \( n \)-alkanes exhibit only orthorhombic modifications. As explained before, the only possible way of packing an odd \( n \)-alkane is with the chains perpendicular to the plane formed by the terminal methyl groups.

\( \text{C}_{19} \) (\( n \)-nonadecane) crystallize in an orthorhombic layered structure [Guillaume et al., 1989]. In this low temperature modification, the \( n \)-alkane molecules exhibit no motion. In the rotator phases, \( R_1 \) and \( R_{11} \) fast translational motions and large amplitude rotation was detected by means of incoherent neutron scattering.

The structure and phase transitions of \( n \)-tritriacontane (\( n \)-C\(_{33}H\(_{68}\)) were investigated by Piesczek et al. [183]. This \( n \)-alkane undergoes two solid-solid phase transformations. The modifications were named A, B, C and D according to occurrence at increasing temperatures. Modification A is the orthorhombic form, \( P_{cam} \) generally found for odd-numbered \( n \)-alkanes. Modifications B and C are monoclinic, and modification D (the rotator phase) approach hexagonal symmetry.

### 5.4.3 Mixtures of \( n \)-alkanes

In order to understand the structural characteristics of waxes, and other products containing long chain molecules of different lengths, it is necessary to consider mixtures of compounds that mimic the composition of these products. The difference in structure induced by mixing can be determined by comparing the structure of the mix to the structures of the pure compounds. Paraffin waxes are mixtures containing mainly \( n \)-alkanes. The behavior of these waxes can be modeled by considering mixtures of \( n \)-alkanes.
A solid solution of n-alkanes is formed if the Gibbs energy of the mixed crystal is lower than that of either of the components. Factors that can affect the solid solubility of n-alkanes include the relative chain lengths of the components and the space groups of the pure compounds [Kitaigorodskii, 1961; Dorset, 1990a]. It was proved [Dorset 1985, 1987] that there is, however, not necessarily a continuity of space group when compounds of the same space group is crystallized, and the molecular conformation formed in the most stable polymorph in the pure compound, is not necessarily the one formed in a solid solution [Craievich, 1984; Dorset, 1990a]. There is, however, a continuity of methylene subcell and type of layer stacking (perpendicular or tilted) in a solid solution.

Generally a mixture of n-alkanes can form a solid solution or a eutectic, depending on the difference in chain lengths. n-Alkanes with a difference in the number of carbon atoms, crystallize in lamella with the chains perpendicular to the plane of the methyl end groups (orthorhombic modification). The packing of chains with different chain lengths has an effect on the lamellar interface. Co-crystallization of n-alkanes with different chain lengths leads to disorder at the surface of the lamella. Due to the difference in chain length, voids are present in the layers [Dorset, to be published]. The presence of non-planar conformations near the terminal groups has been proved spectroscopically [Marconelli, 1982]. The disorder is concentrated at the surface of the molecular end planes, and decreases towards the center of the molecule. This increased disorder near the ends of the chain is modeled structurally by describing the atomic occupancy of the position [Dorset, 1996; Dorset, 1999 to be published].

Two molecular motions correct for the difference in chain length in a solid solution. Firstly, the longitudinal movement of shorter molecules tends to minimize the volume occupied by voids in the layer. Secondly, kinks are present in the longer molecules, shortening the molecule to fit into the layer. The concentration of kinks is higher near the ends of the molecules. This also helps to fill the voids formed as a result of the shorter molecules. The effect of these two motions is the stabilization of the structure by minimizing molecular volume differences.
Solid solution

A solid solution will form if the molecules have similar shapes and sizes, and if one kind of molecule can be replaced by another without significant disturbance of the crystal packing [Kitaigorodskii, 1961]. Within certain limits of relative chain lengths, a solid solution of n-alkanes is formed [Dorset, 1990a].

It is found that such a mixture (molecular alloy) of n-alkanes exhibit orthorhombic symmetry if the difference in chain length of the non-consecutive components is not more than four carbons. The existence of a solid solution can be proved by the regular 00l spacings in the X-ray diffraction patterns as a result of a single average layer spacing.

The Gibbs energy of a solid solution is lower than that of either of its components, and the solid solution is more stable than a mechanical mixture of the components.

Fractionated solid solution

If the difference in chain length is such that formation of a stable solid solution is not possible, a metastable solid solution is formed from the melt. With time spontaneous demixing of components occur, with each lamella formed by a single n-alkane, in contact with other lamellals through the identical planes of the methyl end groups [Dorset, 1986]. Throughout the demixing, a lamellar, orthorhombic subcell structure is maintained. The

![Structure of binary mixture of C_n and C_m after fractionation](image)

Fig 5.2: Structure of binary mixture of C_n and C_m after fractionation
separation most probably occurs by longitudinal rather than lateral diffusion of molecules [Dorset, 1996]. This movement can be visualized as a molecule moving across the gap between lamella into a void in the neighboring lamella.

The layers of pure n-alkanes are stacked randomly, forming a superlattice. It is observed that the structure changes if the relative concentration of the different components change. The degree and rate of demixing is dependant on the difference in chain length between the components and the temperature [Dorset and Snyder, 1995].

**Eutectics**

**Stable eutectic**

Generally the eutectic point for a binary system is nearly at zero concentration for the longer component. At this point a solid solution with random stacking of layers of pure n-alkanes (superlattice) coexist with either the longer or shorter pure component. The structure of the superlattice resembles that of the metastable solution after fractionation. Association of the incommensurate layer structure and the pure n-alkane is possible due to similar terminal methyl planes. The formation of the stable eutectic occurs much faster than the fractionation of the metastable solid solution. The structure stays constant with changing concentration of the components, [Dorset, 1990b] unlike the structure of the metastable solution that changes with relative concentrations of the compounds.

**Insoluble mixture**

If the difference in chain length is so large that no mixing is possible between components, pure n-alkanes exist as separate crystals. The X-ray diffraction pattern shows peaks from both components of the mixture. It is proposed that the paraffins crystallize with the 001 faces on top of each other. If the mixture is cooled form the melt, the higher molecular weight compound crystallize first. The second n-alkane crystallizes on the first, epitaxially directed by identical methyl end group planes in both compounds.
It has been found that with time the components of a mechanical mixture undergo diffusion to form a lamellar structure with mixed chains. This solubilization is thought to be the opposite of fractionation into components to form a eutectic solid.

The fractionation of a solid into an eutectic if the chain length difference is too large is an important concept in the understanding of the molecular dynamics occurring during phase transitions.

5.4.4 Binary Mixtures of n-alkanes

A range can be described from the solid solution to a mixture of the two pure components, depending on factors such as the relative chain length and concentration of the components.

Depending on the crystallization conditions different structures for the same binary mixture can be obtained [Fenrych et al, 1997]. Dorset [1990a] employed electron diffraction to study binary mixtures of n-alkanes. It was found that a binary mixture of n-alkanes could exhibit different structures: a stable solid solution, a structure formed by layers of mixed compounds co-existing with the longer component, and an eutectic formed by a mixture of separated pure components.

Solid solutions

In the literature, only two single crystal structure determinations were reported [Gerson and Nyburg, 1994] for solid solutions of n-alkanes. The structures of the solid solutions of $n$-$C_{24}H_{50}/n$-$C_{26}H_{54}$ and $n$-$C_{20}H_{42}/n$-$C_{22}H_{46}$ were determined from single crystals obtained from $n$-dodecane. For $n$-$C_{24}H_{50}/n$-$C_{26}H_{54}$ the mole fraction of the shorter component was 0.77.

Single crystal data

\[
\begin{align*}
  a &= 4.992 \, \text{Å} \\
  b &= 7.503 \, \text{Å} \\
  c &= 67.448 \, \text{Å}
\end{align*}
\]

Space group $Bb2/m$
The structure can be approximated as a carbon backbone with 27 atoms. The atomic occupancies of the three carbon atoms at the ends of the molecule are less than unity.

The composition of the solid solution of \( n-C_{20}H_{42}/n-C_{22}H_{46} \) was established to be 0.72 fraction of the shorter component.

**Single crystal data**

\[ a = 5.020 \text{ Å} \]
\[ b = 7.711 \text{ Å} \]
\[ c = 58.600 \text{ Å} \]

Space group \( Fmmm \)

The \( n \)-alkane backbone resembles the pure alkane \( n-C_{23}H_{48} \). Atomic occupancies were determined, with the value for the outer carbon atoms less than unity.

A binary mixture of \( n-C_{23}H_{48} \) and \( n-C_{25}H_{52} \) was studied by Retief *et al* [1985]. It was observed that the \( c \) unit cell parameter increases nearly uniformly with increasing percentage of \( n-C_{25}H_{52} \) in the mixture. The \( a \) and \( b \) axis of the binary mixture were larger than for any of the pure compounds. This phenomenon was explained as follows: when a small percentage of short molecules are present, voids are formed and the \( c \)-axis is not shortened. If a large percentage of small molecules are present, the longer molecules have kinks in order to be accommodated in the layer, leading to a decrease in the dimension of the \( c \)-axis.

The structural properties of a solid solution of 1:1 \( n-C_{32}H_{66}: n-C_{36}H_{74} \) was investigated by Dorset [1990a]. In this solid solution it is possible to find microcrystals that resemble both the pure \( n \)-alkane \( n-C_{23}H_{72} \) with space group \( A2_1am \), and the pure \( n \)-alkane, \( n-C_{34}H_{70} \) with spacegroup \( Pca2_1 \). The latter was considered, because the spacegroup of the two pure compounds is also \( Pca2_1 \), eliminating symmetry as a parameter. The structure is described by indicating the fractional coordinates and occupancies of atomic positions. The structure resembles that of pure alkane \( n-C_{34}H_{70} \).
It was found [Dorset, 1985; Dorset, 1987; Dorset, 1990a] that the following binary mixtures form stable solid solutions: $n$-$\text{C}_{32}\text{H}_{66}$/ $n$-$\text{C}_{36}\text{H}_{74}$; $n$-$\text{C}_{33}\text{H}_{68}$/ $n$-$\text{C}_{36}\text{H}_{74}$; $n$-$\text{C}_{38}\text{H}_{78}$/ $n$-$\text{C}_{44}\text{H}_{90}$; $n$-$\text{C}_{44}\text{H}_{90}$/ $n$-$\text{C}_{50}\text{H}_{102}$ and $n$-$\text{C}_{50}\text{H}_{102}$/ $n$-$\text{C}_{60}\text{H}_{122}$. The structure of the odd-even mixture, $n$-$\text{C}_{33}\text{H}_{68}$/ $n$-$\text{C}_{36}\text{H}_{74}$, exhibited ideal mixing, indicating another violation of Kitaigorodskii's law's that state that the solid solution should fractionate.

**Metastable solutions**

The DSC scan of a mixture of $n$-$\text{C}_{30}\text{H}_{62}$ and $n$-$\text{C}_{36}\text{H}_{74}$ changed in shape after the melt crystallized sample was left at room temperature for two days [Dorset, 1986]. When the sample was remelted and crystallized, the DSC scan again resembled the first scan. This behavior indicates the separation of the metastable solution into layers of pure $n$-alkane components. Initially a solid solution is formed from the melt. This solid solution is metastable, and fractionates into orthorhombic layers of pure $n$-alkanes. This stacking of lamella of different chain lengths is possible, since in the orthorhombic modifications the methyl end group planes are identical. Because of random stacking of lamella, the space group symmetry of the individual $n$-alkanes is not retained.

Other binary metastable solid solutions showing fractionation have been reported [Dorset, 1990b]. The odd-even mixture of $n$-$\text{C}_{32}\text{H}_{66}$ and $n$-$\text{C}_{37}\text{H}_{76}$ fractionates at a lower rate than the even-even $n$-$\text{C}_{30}\text{H}_{62}$ and $n$-$\text{C}_{36}\text{H}_{74}$. The combination of $n$-$\text{C}_{28}\text{H}_{58}$/ $n$-$\text{C}_{34}\text{H}_{70}$ fractionates very quickly (a day at room temperature).

**Eutectics**

A 1:1 binary mixture of $n$-$\text{C}_{30}\text{H}_{62}$ and $n$-$\text{C}_{40}\text{H}_{82}$ forms a stable eutectic [Dorset, 1986; , 1997a]. A pure eutectic component of the longer chain, $n$-$\text{C}_{40}\text{H}_{82}$ could be observed, exhibiting an electron diffraction pattern with orthorhombic space group $Pca2_1$. The superlattice structure could also be observed. The domains of superlattice and pure $n$-$\text{C}_{40}\text{H}_{82}$ can associate via identical terminal methyl group planes. The structure of the eutectic is not influenced by temperature or aging, and is constant for all relative concentrations of components.
5.4.5 Tertiary mixtures of \( n \)-alkanes

The structure of a mixture of three \( n \)-alkanes (\( n\)-C\(_{36}\)H\(_{74}\), \( n\)-C\(_{38}\)H\(_{78}\) and \( n\)-C\(_{40}\)H\(_{82}\)) was investigated by Dorset [to be published]. The sample was obtained by epitaxial orientating an equimolar mixture of the \( n \)-alkanes on benzoic acid. The formation of a solid solution was indicated by a single layer repeat in the electron diffraction pattern. The structure was similar to that of pure \( n\)-C\(_{39}\)H\(_{80}\). The unit cell dimensions were \( a = 7.42 \, \text{Å} \), \( b = 4.96 \, \text{Å} \) and \( c/2 = 50.9 \, \text{Å} \). Systematic absences were indicative of either space groups \( Aa \) or \( A2_1am \). Fractional occupancies were determined for the outermost carbon atoms.

5.4.6 Multicomponent mixtures

The correlation between the long \( c \) parameter and the composition of \( n \)-alkane mixtures was highlighted by Chevallier \textit{et al} [1999]. Two quaternary alloys of equimolar amounts of C\(_{22}/C_{26}/C_{30}/C_{34}\) (1) and C\(_{24}/C_{28}/C_{32}/C_{36}\) (2) as well as three commercial products consisting of 23 and 33 consecutive \( n \)-alkanes with chain lengths between 20 and 52 carbons were investigated using X-ray diffraction.

In mixture (1) two series of (001) diffraction lines were observed indicating the presence of two orthorhombic solid solutions, and in mixture (2) three (001) series indicating three orthorhombic solid solutions. The diffractograms from the commercial products showed only one series of (001) diffraction peaks due to the presence of a single molecule layer stacking periodicity in the long \( c \)-axis direction, and thus one orthorhombic crystalline phase.

It was also found that the long spacings of each mixture is representative of the chain length of a hypothetical orthorhombic pure C\(_n\). The periodicity of the layers in the molecular alloys is equal to the average length of C\(_n\) chains with an excess value of 1.5 carbon atoms. This excess value is probably due to conformational disorder of the stacking of the chains. The molecules with carbon numbers greater than \( n \) of the hypothetical orthorhombic pure C\(_n\) must be bent to be inserted in the layers. These bends disturb the lamellar surface. If there isn't a continuous distribution of chain lengths in \( n \)-alkanes, or when there is more than four carbon atoms difference in non-consecutive \( n \)-
alkanes, the unit cell cannot accommodate all the voids, and a single solid solution cannot be formed. In this case the system forms more than one orthorhombic solid solution, or even an amorphous solid if the chain lengths vary too much. These molecular alloys transforms to the rotator phase just below melting point [Chevallier et al, 1999]. With increasing temperature, the R₁ phase (Fmmm) is formed first, changing into the R₁l phase (R3m).

Defect chain motions in mixtures of n-alkanes were highlighted by an investigation of mixtures with average chain lengths of 28.1, 28.3 and 28.9 by X-ray powder diffraction and NMR [Basson & Reynhardt, 1992]. No splitting of peaks in the X-ray powder diffractograms were observed, indicating the formation of homogeneous solid solutions. Three types of motions have been observed in the mixtures, threefold reorientations of the methyl groups, gauche defect motions of the end of the long chains, and twofold screw reorientations exhibited by the shorter chains. It was indicated that the concentration of these defects is higher in binary mixtures than in pure n-alkanes.

5.5 X-ray Diffraction

Except for n-alkanes with triclinic symmetry, diffraction patterns of these molecules are the result of scattering from the full cell superimposed on diffraction from the subcell. The (00l) reflections occurring at low angles, demonstrate the lamellar structure of an n-alkane, as well as the intra-lamellar spacing.

n-Alkanes usually crystallize in thin plates as a consequence of their layered structure, typically only a few hundred μm thick. They tend to twin across the (00l) planes. Preferred orientation can present a serious problem if a flat sample holder is used in powder diffraction. A more random sample can be obtained by using a glass capillary as sample holder.

For an isostructural group of paraffins the diffraction patterns are uniform. The 00l peaks, appear in the region 0° < 2θ < 16°. The 110 and 020 peaks are found in the region 20° < 2θ < 25°.
5.6 Molecular modeling

McGann and Lacks [1998] demonstrated that the interlamellar spacing is independent of chain length by using Monte Carlo simulations to investigate the effect of thermal motion on structure. A one-dimensional model was used with nearest-neighbors in the same chain interacting through a harmonic potential, and neighbors in different chains interacting through a Lennard-Jones potential. The simulations were performed at constant temperature (increasing temperatures up to melting temperature for each system) and zero pressure, with sixteen chains in the simulation cell. Chain lengths from 10 to 200 carbon atoms were simulated and for all simulations no significant chain length dependence was found for the interlamellar spacing. This independence is due to the fact that intrachain vibrations that tend to increase the interlamellar spacing in longer chains, is cancelled out by interchain vibrations that act to decrease the interlamellar spacing in longer chains.

5.7 Conclusion

Various lamellar packings of \( n \)-alkane molecules are possible. These are

<table>
<thead>
<tr>
<th>Hexagonal</th>
<th>Chains perpendicular to end group planes.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orthorhombic</td>
<td>Chains perpendicular to end group planes. Subcell orthorhombic.</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>Chains tilted relative to end group planes. Subcell orthorhombic.</td>
</tr>
<tr>
<td>Triclinic</td>
<td>Chains tilted relative to end group planes. Subcell triclinic.</td>
</tr>
</tbody>
</table>

The presence of impurities, for example, neighboring homologues has caused a great deal of confusion in the early studies of \( n \)-alkanes. Early reports of structures may suffer
from the inability to purify $n$-alkanes from other, similar long chain compounds. The presence of these impurities has an adverse effect on the structure, resulting in uncertainty about the reliability of these early reports.
Chapter 6

Fatty Acids

Thibaud and Dupre La Tour discovered the polymorphism of fatty acids in 1930. Since then the polymorphism and crystallography of fatty acids have been investigated and reported in various publications in the literature [von Sydow, 1955; Gunstone, 1976; Garti and Sato, 1988]

Because the field is well investigated, only a brief overview of the crystallographic characteristics and occurrences of fatty acids will be given. The presence of fatty acids in various natural products, especially waxes, indicates the need to sufficiently understand the structural behavior of fatty acids to be able to predict changes in properties induced by changes in structure.

Fatty acids were probably one of the first groups of long chain molecules investigated, and nomenclature used by early researchers is still encountered today. One example is the non-IUPAC naming of long chain derivatives still found in the literature and used in certain industries:

<table>
<thead>
<tr>
<th>Chain length</th>
<th>IUPAC Name</th>
<th>Trivial Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Hexanoic</td>
<td>Caproic</td>
</tr>
<tr>
<td>7</td>
<td>Heptanoic</td>
<td>Enanthic</td>
</tr>
<tr>
<td>8</td>
<td>Octanoic</td>
<td>Caprylic</td>
</tr>
<tr>
<td>9</td>
<td>Nonanoic</td>
<td>Pelargonic</td>
</tr>
<tr>
<td>10</td>
<td>Decanoic</td>
<td>Capric</td>
</tr>
<tr>
<td>11</td>
<td>Hendecanoic</td>
<td>Undecanoic*</td>
</tr>
<tr>
<td>12</td>
<td>Dodecanoic</td>
<td>Lauric</td>
</tr>
<tr>
<td>13</td>
<td>Tridecanoic</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Tetradecanoic</td>
<td>Myristic</td>
</tr>
<tr>
<td>15</td>
<td>Pentadecanoic</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Hexadecanoic</td>
<td>Palmitic</td>
</tr>
<tr>
<td>17</td>
<td>Heptadecanoic</td>
<td>Margaric</td>
</tr>
<tr>
<td></td>
<td>Name</td>
<td>Systematic Name</td>
</tr>
<tr>
<td>---</td>
<td>--------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>18</td>
<td>Octadecanoic</td>
<td>Stearic</td>
</tr>
<tr>
<td>19</td>
<td>Nonadecanoic</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Eicosanoic</td>
<td>Arachidic</td>
</tr>
<tr>
<td>21</td>
<td>Heneicosanoic</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>Docosanoic</td>
<td>Behenic</td>
</tr>
<tr>
<td>23</td>
<td>Tricosanoic</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>Tetracosanoic</td>
<td>Lignoceric</td>
</tr>
<tr>
<td>25</td>
<td>Pentadecanoic</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>Hexacosanoic</td>
<td>Cerotic</td>
</tr>
<tr>
<td>27</td>
<td>Heptacosanoic</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>Octacosanoic</td>
<td>Montanic</td>
</tr>
<tr>
<td>29</td>
<td>Nonacosanoic</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>Triacontanoic</td>
<td>Melissic</td>
</tr>
</tbody>
</table>

*This name is another systematic name occurring in the literature.*

Because properties of different polymorphs of a compound may differ, the identification, characterization and control of the polymorphism of fatty acids and fatty acid derivatives play an important role in industries where these compounds are frequently encountered. Products that contain fatty acids include cosmetics, pharmaceuticals, polishes and food products. The crystallization of fatty acids in these products will cause customer dissatisfaction.

The structural behavior of all natural derivatives of fatty acids can only be described once the structural properties of pure fatty acids is understood. A collective term for the natural derivatives of fatty acids is lipids, and these include glycerides, waxes and phosphoglycerides. In natural products fatty acids and long chain alcohols can form esters or amides, and the hydrolysis products of fatty acids include long chain aldehydes, long chain alcohols, and various carbohydrates.
6.1 Occurrence of normal fatty acids in natural products

In this chapter C_{n} refers to a normal fatty acid with n the number of carbon atoms in the molecule. Fatty acids in the range C_{4} – C_{10} occur in milk and seed fats. n-Decanoic acid (C_{10}) is a major fatty component (60%) in elm seed. n-Dodecanoic (C_{12}) acid is found in cinnamon oil (80 – 90%), coconut oil (45 – 50%) and palm kernel oil (45 – 55%). n-Hexadecanoic acid (C_{16}) is present in almost every fatty product that has been investigated, and is the most widely occurring saturated acid. This acid is a component of fish oils (15 – 20%), fats of land animals (25 – 30%), cottonseed oil (22 – 28%), other vegetable fats and palm oil (35 – 40%). n-Octadecanoic acid (C_{18}) is less common than palmitic acid, but a major component of cocoa butter (35%), and found in most animal fats. It is clear that nature prefers an even number of carbon atoms in the fatty acid chain, but odd acids are sometimes found in natural products. For example the range of odd acids C_{13} – C_{19} are found in fish oils, and C_{9} – C_{23} in certain vegetable fats. It is important to note that these odd acids do not often exceed 1-2% of the total, and are usually present in an even lower percentage.

Why is preference given to the formation of even numbered fatty acids in nature? Are these products easier to synthesize in organisms, or is the reason deeper lying and related to the structural differences between odd and even numbered fatty acids causing differences in the functions of bio-structures? To answer these questions, many gaps in present research will still have to be filled before a global answer may be discovered.

6.2 Crystallography of fatty acids

The odd even effect is the main factor determining the structure of fatty acids. From single crystal structure point, the fatty acid structures for even and odd acids have been divided into sub groups depending on the different packing of molecules. For each isostructural series, there is a linear relationship between the long spacing and the number of carbon atoms in the chain. An important factor influencing the packing of fatty acid
molecules is the ability to form hydrogen bonds between the carboxyl groups. This results in a lamellar packing of molecules.

6.2.1 Even saturated fatty acids

In the case of even fatty acids the four different polymorphic forms encountered are called A, B, C and E. This nomenclature was derived from the different tilt angles of the molecules relative to the plane formed by the carboxylic groups. Form A shows the smallest tilt, and form E the highest – leading to a decrease in long spacing from the A form down the series. This is not the only nomenclature used to describe different crystal forms of fatty acids. Alternatively the system for glycerides is used: the hydrocarbon chain packing is described by the symbols α, β and β'. If two crystal forms have the same hydrocarbon packing, subscripts are added, numbered in the order of decreasing melting point. This nomenclature is not used often, and we will refer to the polymorphs as A, B, C or E.

The polymorphism of even fatty acids can be described by the following figure:

\[
\begin{array}{c}
\text{liquid} \\
\downarrow \uparrow \\
\text{A} \rightarrow \text{B} \rightarrow \text{C} \\
\downarrow \uparrow \\
\text{Solvents}
\end{array}
\]

The C – form is the most stable form at high temperatures, and the A to B to C transition is irreversible.

The specific polymorph formed depends on the purity of the sample, temperature of crystallization and method of crystallization (by evaporation, from the melt etc.)
A form

*n-Dodecanoic acid - C$_{12}$ (Lauric acid)*

The A crystal form of *n*-dodecanoic acid was investigated by von Sydow [1955], who named this form the A-super form because he regarded it as a sixfold superstructure from the packing of the chains. The single crystal structure of the A-super form of *n*-dodecanoic acid was determined [Goto and Asada, 1978a] and exhibited a peculiar packing of fatty acid molecules. Instead of the expected packing of molecules that form a plane of carboxyl groups the *n*-dodecanoic acid molecules exhibits two types of molecular conformations: the type normally found in the A$_1$ structure, and another conformation with the carboxyl group rotated about the C1-C2 bond.

Fig 6.1. Projection of A$_1$ structure of *n*-dodecanoic acid on $ac$-plane [Goto and Asada, 1978a].

*Single crystal data:*

Triclinic

\[ a = 4.33 \, \text{Å}, \quad b = 5.42 \, \text{Å}, \quad c = 2.52 \, \text{Å} \]

\[ \alpha = 75.9^\circ, \quad \beta = 108.9^\circ, \quad \gamma = 122.1^\circ \]

\[ Z = 12 \]
Carboxyl groups and terminal methyl groups both occur in the same lamellar interface, with three molecules with their carboxyl groups in the same direction, and the next three molecules with their carboxyl groups facing in the direction opposite to the first three. Crystallographically different molecules can be identified—I, II and III, with II and III almost geometrically equivalent. If both molecules had the same conformation, the O4-O2 distance would be too short to form a hydrogen bond between these two molecules. By rotating the carboxyl group, the distance between the molecules is increased, and a hydrogen bond becomes possible.

The $A_1$ form of lauric acid has a structure similar to the A-super form, and is triclinic with two molecules per unit cell [Lomer, 1963].

**Single crystal data:**

Triclinic

\[
\begin{align*}
a &= 7.45 \text{ Å}, \\
b &= 5.40 \text{ Å}, \\
c &= 17.47 \text{Å} \\
\alpha &= 96.88^\circ, \\
\beta &= 113.13^\circ, \\
\gamma &= 81.12^\circ
\end{align*}
\]

The unit cell of the $A_1$ form fits exactly with a three times larger cell of the A-super form. The difference between the two A-form structures can be explained by the translation of the molecules indicated by arrows in Fig 6.1. If these two molecules are translated to the next lamella, the $A_1$-form can be obtained from the A-super form. In both the $A_1$ and A-super forms the hydrocarbon chains are packed according to the T// subcell.

**B-form**

The structure of the B-form of $n$-octadecanoic acid was redetermined [Goto and Asada, 1978b] after it was proved that the conformation of the carboxyl groups was previously incorrectly determined.
Single crystal data:
Monoclinic
\[ a = 5.587 \text{ Å}, b = 7.386 \text{ Å}, c = 49.33\text{Å} \]
\[ \beta = 117.24^\circ \]
\[ Z = 4 \]

Fig 6.2. Projection of B form of n-octadecanoic acid on the ac-plane [Garti and Sato, 1988]

The bond between the second and the third carbon display a gauche conformation, instead of an all-trans conformation. Carboxyl groups are in the same layer, with hydrogen bonds between a pair of molecules causing a dimer to form. The hydrocarbon subcell is orthorhombic.

A B-form of n-octadecanoic acid different from the one previously reported displays a polytypic structure [Kobayashi et al, 1984; Kaneko et al, 1994]. Two bimolecular layers are stacked on one another, with one layer having the same structure of the ordinary B-form that was reported earlier.
Fig 6.3. Polytypic structure of B-form of n-octadecanoic acid [Kaneko et al, 1994].

**Single crystal data:**

Orthorhombic

\[ a = 7.404 \text{ Å} \quad b = 5.591 \text{ Å} \quad c = 87.662 \text{Å} \]

\[ Z = 8 \]

Space group \( Pbca \)

The bimolecular layers are related to each other by a two-fold \( c \)-screw axis operation. The arrangement of terminal methyl groups differs from the arrangement in the B-form, and the distances between methyl groups at the lamellar interface differ from that found for the B-form.
C-Form

The structure of the C-form of \( n \)-dodecanoic acid (C\(_{12} \)) resembles that of the B-form. Both forms display dimers, but in the C-form the chains are in the extended, all-\textit{trans} conformation.

The dependence of the unit cell dimensions of this monoclinic form on the number of carbon atoms in the chain was reported \[Abrahamsson and von Sydow, 1954\]. The \( a \) and \( b \) axes and the angle \( \beta \) decreases asymptotically with increasing chain length, and the \( c \) axes and long spacings, \( d \) (001) increases linearly.

\[ \text{Fig 6.4: C form of } n \text{-dodecanoic acid [Garti and Sato, 1988].} \]
E-form

The E-form represents a metastable phase, with chains in an all-trans conformation, similar to that of the C-form. The structure of the E-form of n-octadecanoic acid (C₁₈) was reported [Kaneko et al, 1990] as monoclinic with the chains in an all-trans conformation.

Fig 6.5: Projection of E-form of n-octadecanoic acid [Kaneko et al, 1990].

**Single crystal data:**

Monoclinic

\[
a = 5.603 \text{ Å}, b = 7.360 \text{ Å}, c = 50.789 \text{Å}
\]

\[
\beta = 119.40^\circ
\]

\[
Z = 4
\]

\[P2_1/a\]

Similar to the polytypic B-form of n-octadecanoic acid, a polytypic E-form was found [Kaneko et al, 1994] to consist of layers of the E form stacked onto one another, and related to each other by a two fold c-screw operation.
Fig. 6.6: Projection of orthorhombic polytype of the E form of n-octadecanoic acid [Kaneko et al, 1994].

**Single crystal data:**

Orthorhombic  
\[ a = 7.389 \, \text{Å} , b = 5.609 \, \text{Å} , c = 88.41 \, \text{Å} \]

\[ Z = 8 \]

Space group \( \text{Pbca} \)

**Phase transitions**

There are not many reports in the literature on structural changes occurring during solid-state phase transitions of fatty acids. One solid state transformation that has been investigated is that of the irreversible change of \( n \)-octadecanoic acid (stearic acid) from the E-from to the C-form [Kaneko et al, 1992]. In the case of \( n \)-octadecanoic acid, the C form is stable above 32° C, and the A, B and E-forms undergo an irreversible transformation to the C-form upon heating. By means of polarized infrared and X-ray diffraction methods, it was deduced that although the external shape and optical transparency of the crystal stay unchanged during the phase transition, large displacements of the alkyl hydrocarbon chains occur.
Both the E and the C-forms of $\text{n-octadecanoic acid}$ are monoclinic with space group $P2_1/\alpha$, but the structures differ in the orientation of the hydrocarbon subcell against the main lattice.

The following observations were made regarding the solid-state transition:

- The direction of the $c^*$ axis remained virtually unchanged — despite the decrease in thickness of the lamella, the orientation of the interlamellar surface does not change.

---

**Fig. 6.7:** Molecular conformation of E-form and C-form of $\text{n-octadecanoic acid}$ relative to lattice [Kaneko et al, 1992].
A rotation of the unique $b$ axis occurred – in half of the samples the axis rotated by an angle of between 160° - 180° (case 1) and in the other half by an angle in the range of 60° - 90° (case 2).

During this solid state transition the orientation of the hydrocarbon subcell changes from the (011) type to the (201) type. The following mechanisms for this transition were proposed:

- Translational displacement of the molecules in the direction of the molecular axis. This leads to reconstruction of the lamellar interface resulting in an interlamellar surface that is not parallel to the original.
Increase in tilt angle of the molecules relative to the interlamellar layer. The lamellar stacking stays unchanged. If the tilt angle increase from 27° to 35°, the alkyl chains must slip past each other by two methylene groups between unit cells.

Because the bulky carboxyl group will experience difficulty in penetrating the subcell of the hydrocarbon chains, the last mechanism seems more plausible for the form E to form \( \mathbb{C} \) transition of \( n \)-octadecanoic acid.

**Crystallization of a specific polymorph**

During the growth of crystals in solution, polymorphic transformations may occur [Kaneko *et al.*, 1994]. During the crystallization process of B and E forms of \( n \)-octadecanoic acid, the single layered polytype of the E form crystallized first, and was overgrown on the (001) face with the double layered polytype of form E. For certain single crystals a polymorphic transformation from form E to form B occurred – the single layered polytype of form B grew by consuming crystals of the unchanged E form by solution mediated polymorphic transformation. Thus, the crystallization of form B directly from solution does not occur, instead crystals of form B form by heterogeneous nucleation on the (001) face of a crystal in the E form, which undergoes a phase transition to the B form. During this transformation the crystal shape and transparency did not change because the molecular conformation remains virtually the same, except for a change in conformation in the vicinity of the carboxyl group.
6.2.2 Odd saturated fatty acids

The figure summarizes the polymorphic behavior of odd fatty acids. All forms can be obtained from solvents, but only the B’ form from the melt.

The C’-form is stable in a small temperature range just below the melting point. The B’-form is the most stable form, except for just below the melting point.

A’-form

The crystal structure of n-pentadecanoic acid was reported in only one projection [von Sydow, 1954] as dimers packed in an all-trans fashion. All the carboxyl groups are hydrogen bonded and in one plane. The space group is *P1*, with two molecules in the unit cell.
More recently the single crystal structure of the A’ form of n-tridecanoic acid was reported [Goto and Asada, 1980]. This structure is similar to that found for n-pentadecanoic acid, with the molecules packed in an all-trans conformation. The packing of hydrocarbon chains is triclinic, T\(\text{II}\).

**Single crystal data:**
Triclinic
\[
as = 4.273 \, \text{Å}, b = 4.972 \, \text{Å}, c = 37.686 \, \text{Å}
\]
\[
\alpha = 90.36^\circ, \beta = 109.44^\circ, \gamma = 112.43^\circ
\]
\(Z = 2\)
\(P1\)

**B’-form**
In the B’-form of n-pentadecanoic acid [von Sydow, 1956] the molecules are packed in an all-trans configuration.
Fig. 6.9: Projection of B’ form of n-pentadecanoic acid [Garti and Sato, 1988].

**Single crystal data:**

Triclinic

\[ a = 5.543 \, \text{Å}, \quad b = 8.061 \, \text{Å}, \quad c = 42.58 \, \text{Å} \]

\[ \alpha = 114.3^\circ, \quad \beta = 114.22^\circ, \quad \gamma = 80.62^\circ \]

\[ Z = 4 \]

Space group \( P1 \) or \( P\bar{1} \)

The hydrocarbon packing is orthorhombic \( O_\perp \), and the main difference between the A’ and the B’-forms is that the B’-form exhibits a larger tilt angle.

A single crystal structure determination of \( n \)-heptadecanoic acid in the B’-form has been reported [Goto and Asada, 1984]. The \( n \)-heptadecanoic molecules are in the all-trans conformation, with an orthorhombic hydrocarbon subcell.
Single crystal data:
Triclinic
\(a = 5.561 \, \text{Å}, b = 8.018 \, \text{Å}, c = 47.9 \, \text{Å}\)
\(\alpha = 114.18^\circ, \beta = 114.96^\circ, \gamma = 80.22^\circ\)
\(Z = 2\)
Space group P 1

C'-form

Fig 6.10 shows a projection of the crystal structure of the C'-form of \(n\)-undecanoic acid.

Single crystal data:
Monoclinic
\(a = 9.622 \, \text{Å}, b = 4.915 \, \text{Å}, c = 34.18 \, \text{Å}\)
\(\beta = 131.29^\circ\)
\(Z = 4\)
\(P2_1/\alpha\)

Fig 6.10: Projection of C' form of \(n\)-undecanoic acid [Garti and Sato, 1988].
A distortion towards a hexagonal conformation is probably due to the narrow temperature range of the C'-form. The hydrocarbon chain subcell is orthorhombic O$_1$.

6.3 Odd-even effect

Scanning tunneling microscopy (STM) studies were performed on monolayers of fatty acids with various chain lengths, to shed more light on the cause of the odd-even effect at microscopic level [Hibino et al, 1998]. The molecules form dimers via hydrogen bonding between the carboxyl groups and the alkyl chains lie parallel to the graphite surface. The three dimensional structure is reduced to a two dimensional monolayer structure on the surface. For the even numbered fatty acids, a mirror plane was observed with left and right handed structures being present. No mirror plane was seen for odd numbered fatty acids. Because of the asymmetry of the carboxyl group, fatty acids are chiral in two dimensions, but this effect is cancelled in three dimensions so that fatty acids become achiral in a crystal structure. Thus, for even numbered fatty acids the monolayer formed on graphite consists of two types of domains, each consisting of molecules of a specific enantiomer. However, the odd numbered fatty acids exhibits a two-dimensional structure that is a racemic mixture of two types of enantiomorphic dimers. The unit cell for the structure of the monolayer of odd-numbered fatty acids is formed by 2 X 2 molecules parallel and perpendicular to the molecular axis, and four fatty acid molecules in a unit cell, whereas the unit cell for the even-numbered fatty acids is constructed by 2 X 1 molecules, with the cell containing two molecules.

The arrangement of end methyl groups and carboxyl groups is essentially the same for both the even- and the odd-numbered fatty acids, but the dimer as a whole is different. The extra carbon in the odd numbered acid gives rise to a change in the position of the carboxyl group relative that found for the even acids. This effect brings about a difference in cohesion energy between the even and the odd fatty acid molecules, and become evident in what is referred to as the odd-even effect.
Fatty acids are used as additives in various products, improving the properties of the pure compound. By varying the chain length of the acid used, various properties of the resulting crystal such as melting point and solubility can be fine-tuned. An example is the complex formed by equimolar amounts of \( n \)-octadecanoic acid and nicotinamide [Amai \textit{et al}, 1998].

Complexing the pharmaceutical agent with a fatty acid leads to improved hygroscopicity. Depending on the number of carbon atoms in the fatty acid, the nicotinamide is released from the complex at a definite temperature and pH. In this complex the alkyl chain of \( n \)-octadecanoic acid exhibits an \textit{all-trans} conformation, similar to the C and the E forms.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{odd_even_unit_cell.png}
\caption{Difference in unit cell for odd and even fatty acids [Hibino \textit{et al}, 1998].}
\end{figure}
6.4 Conclusion

The occurrence of fatty acids in natural waxes and other products clearly makes the investigation of the structural behavior of fatty acids an important research field. The possibility of hydrogen bond formation that is encountered in the fatty acids is also present in waxes with oxygen containing molecules, for example oxidized wax and various plant waxes.

This system indications the complex polymorphism exhibited by long chain molecules.
Chapter 7

*n-Alkylammonium halides* $(\text{C}_n\text{H}_{2n+1}\text{NH}_3\text{X}, \ X = \text{Cl, Br, I})$

*n-Alkylammonium halides* have applications as surfactants, emulsifiers, lubricants, bactericides and detergents.

These molecules are not only of interest in material science, but also in life sciences as they are commonly used as models for cell membranes [Ringsdorf *et al*, 1988] to aid in the understanding of membrane structure. Amphiphilic molecules like *n*-alkylammonium halides are building blocks for self-organizing systems. Within the cell membrane the amphiphilic molecules self-organize to form bilayers. Mobility through the membrane is determined by the structure of the membrane. Phase transitions in the membrane are due exclusively to the normal hydrocarbon part of the membrane. To investigate the structure property relationships of membrane components, it is necessary to investigate model membranes like *n*-alkylammonium halides that also crystallize in bilayers.

Rodlike amphiphilic entities called mesogens, like *n*-alkylammonium halides do not transform directly from the crystalline phase to the isotropic liquid state. Intermediate liquid crystalline phases are formed, combining the order of the crystalline state with the mobility of the liquid phase. Generally the mesogens are orientated parallel to each other, resulting in long-range order. Smectic or nematic systems can be formed. In the smectic phase the mesogens are arranged in layers. The smectic phase can be divided into states where the mesogens are perpendicular to the layers or tilted by various angles to the layers. In the nematic phase the mesogens are isotropically distributed.

In *n*-alkylammonium halides, the carbon chains together with the ammonium group and halide anion function as a mesogen. The molecules organise to form an ordered, lamellar structure, similar to a smectic phase. The anisotropic molecules lead to anisotropic properties in their crystals.
In this section the following nomenclature will be used to refer to \( n \)-alkylammonium halides: \( C_n\text{Br} \) indicates an \( n \)-alkylammonium bromide where the normal alkyl group is comprised of \( n \) carbon atoms, similarly, \( C_n\text{Cl} \) refers to the chloride salt.

### 7.1 Phase transitions of \( n \)-alkylammonium halides:

\[
\begin{align*}
\text{Hexagonal} & \quad \alpha \text{ phase} \\
& \quad \downarrow \\
\text{Orthorhombic} & \quad \beta \text{ phase} \\
& \quad \downarrow \\
\text{Orthorhombic} & \quad \delta \text{ phase} \\
& \quad \downarrow \\
\text{Interdigitated} & \quad i \text{- phase} \\
& \quad \leftarrow \\
\text{Ground state} & \quad \text{Metastable} \\
& \quad \varepsilon \text{ phase} \\
& \quad \text{non-interdigitated}
\end{align*}
\]

**Fig. 7.1.** Phase transitions of \( n \)-alkylammonium halides

\( n \)-Alkylammonium halides undergo a complex series of solid state transitions with increasing temperature [Tsau and Gilson, 1972; Tsau and Gilson, 1974]. For \( n \)-alkylammonium chlorides with 10 or more carbon atoms in the chain, the phase formed from crystallisation at room temperature is either monoclinic (interdigitated or
i-phase) or orthorhombic (δ-phase) [Libscomb & King, 1950]. A sample crystallised at room temperature that has not been heated above the lowest transition temperature is said to be in a “primary” phase. Upon heating the long spacings increase, and a solid state transition to a hexagonal phase, space group $P4/nmm$ occurs. When cooled to room temperature the crystal does not return to the original primary phase, but forms a secondary monoclinic phase, with a larger long-spacing than that of the primary phase. This irreversible transition is probably due to two possible crystal packings with similar energies, but a large activation energy to convert from one form to another. It can also be a result of the rapid crystallisation causing the “freezing in” of disorder.

### 7.2 Structural investigations:

Researchers became interested in the structural aspects of $n$-alkylammonium halides as early as the 1930’s. In 1932 Bernal determined the unit cell dimensions and possible space groups of the room temperature polymorph of $n$-octadecylammonium chloride, and investigated the optical properties of this compound. The fact that the layers of this compound slope in opposite directions was confirmed optically.

In 1950 Clark and Hudgens investigated the structures of normal alkylammonium halides by means of X-ray photographic techniques. Cell dimensions were determined, and it was concluded that the low temperature modifications of $C_nCl$ with $n$ even exhibit monoclinic symmetry with space group $P2_1$ or $P2_1/m$. $n$-Tridecylammonium chloride was found to be orthorhombic with space group $C2ca$ or $Cmca$.

Gilson et al [1975] observed a discontinuity in the long spacings in going from 16 carbon atoms in the $n$-alkylammonium chlorides to 17 carbon atoms in the chain. This indicates a change in the packing – the change from the interdigitated to the non-interdigitated structure from crystallisation at room temperature. It can thus be said that from $n$-heptadecylammonium chloride and higher the structure is non-interdigitated at room temperature. How can this be explained? This means the effective chain diameter for the longer chains, $n>16$, is too large at room temperature
for an interdigitated structure to form. The longer the chain, the higher the energy and more disorder the molecule has at a specific temperature. With increasing chain length, the carbon atoms towards the end of the molecule posses more disorder than those closer to the ionic layer.

At room temperature, the \( n \)-alkylammonium chlorides are tetragonal up to a chain length of 9 carbons, monoclinic for hydrocarbon chain length of 12, 14, 15, 16 and orthorhombic for chains 13 and 18. Transitions occur below room temperature for chain length up to 9 and above room temperature from a chain length of 10.

For \( n \)-alkylammonium chlorides, \( n > 9 \) and \( n < 17 \), the room temperature structure is interdigitated. For \( n = 9 \) [Reynhardt and Wozniak, 1993] the structure formed at room temperature is not interdigitated, and found to be the \( \beta \) phase. Interdigitation starts if the sample is cooled from room temperature, but a fully interdigitated state is never reached.

### 7.2.1 Low temperature polymorph — interdigitated phase

The lowest energy polymorph, phase i, is an interdigitated layered structure and is sometimes referred to as the low temperature structure. The interdigitated structure consists of polar and non-polar layers. The polar layers are formed by alternating ammonium and halide ions held together by hydrogen bonds. Each N atom forms a hydrogen bond with three halide ions, and each halogen ion is hydrogenbonded to three \( \text{NH}_3 \) ions. The adjacent \( n \)-alkylammonium halide ions are bonded via N-H...Cl bonds to two different chlorine layers.

The non-polar layers consist of parallel hydrocarbon chains attached by van der Waals forces. Covalent N-C bonds link the polar and non-polar layers.
Fig 7.2 Interdigitated structure of \( n \)-decylammonium chloride [Schenk and Chapuis, 1986]

\( n \)-Alkylammonium chlorides:

In the literature only three single crystal structures of interdigitated \( n \)-alkylammonium chlorides with more than 10 carbon atoms in the chain have been reported, that of \( n \)-decylammonium chloride (\( \text{C}_{10}\text{H}_{21}\text{NH}_{3}\text{Cl} \)) [Schenk and Chapuis, 1986], \( n \)-undecylammonium chloride monohydrate (\( \text{C}_{11}\text{H}_{23}\text{NH}_{3}\text{Cl}.\text{H}_{2}\text{O} \)) and \( n \)-dodecylammonium chloride (\( \text{C}_{12}\text{H}_{25}\text{NH}_{3}\text{Cl} \)) [Silver and Marsh, 1995].

\( n \)-Decylammonium chloride (\( \text{C}_{10}\text{H}_{21}\text{NH}_{3}\text{Cl} \))

The hydrocarbon part of \( n \)-decylammonium chloride at room temperature is similar to a smectic lipid bilayer [Kind \textit{et al}, 1982].

This interdigitated structure was solved from data of a single crystal grown from a mixture of ethanol and diethyl ether, collected at room temperature [Schenk and Chapuis, 1986].
Fig 7.3: Packing of n-decylammonium chloride [Schenk and Chapuis, 1986].

**Single crystal data:**

Monoclinic

\[
a = 5.6996 \text{ Å}, \quad b = 7.1638 \text{ Å}, \quad c = 15.490 \text{ Å}
\]

\[
\beta = 91.297^\circ
\]

\[Z=2\]

Space group \(\text{P}2_1\)

The chains are tilted at the following angles to the unit cell axes \(a\), \(b\) and \(c\): \(\varphi_a=65^\circ\), \(\varphi_b=89^\circ\) and \(\varphi_c=26^\circ\), with the C and N atoms forming a nearly perfect plane. The alkyl chains of the molecule packs in an orthorhombic subcell with \(a_s=7.16\ \text{Å}\), \(b_s=5.18\ \text{Å}\), \(c_s=2.56\ \text{Å}\) and space group \(\text{Pbnm}\), packing \(O_b\) according to the article by Segerman [1965]. The area of each chain was found to be \(18.5 \text{ Å}^2\).

**n-Undecylammonium chloride monohydrate (C\(_{11}\)H\(_{23}\)NH\(_3\)Cl.H\(_2\)O)**

The structure of the first \(n\)-alkylammonium halide [Silver et al, 1996] containing a solvent molecule indicated the existence of a new type of polymorphism in \(n\)-alkylammonium halides, namely pseudomorphism.

Single crystals were grown from a mixture of an aqueous ferrous chloride solution and ethanol. In the literature no explanation was given as to why the iron salt was added, and what effect this has on the packing and incorporation of water into the structure. No reply was received from the author on the reasons for using ferrous chloride. This is definitely a subject worth investigating in future work - the effect of the presence of metal salts on the packing of \(n\)-alkylammonium halides.
Data was collected at reduced temperature probably to inhibit the loss of water molecules from the structure, but no indication of the exact temperature was given.

![Diagram](image)

**Fig 7.4:** Packing of n-undecylammonium chloride [Silver *et al.*, 1996]

**Single crystal data:**
Monoclinic  
\[ a = 7.701 \text{ Å}, \quad b = 40.020 \text{ Å}, \quad c = 4.6437 \text{ Å} \]
\[ \beta = 107.34^\circ \]
\[ Z = 4 \]
Space group \( P2_1/a \)

The water molecule is hydrogen bonded to both the Cl and the N atoms. The chains are not fully extended, but distorted to accommodate the water molecule in the structure. The polar layer in the lamellar structure is formed by the N, Cl and O atoms, and the non-polar layer by the normal alkyl chains. The closeness of the O and Cl atoms indicates the possible existence of hydrogen bonding between the atoms - 3.180 and 3.226 Å respectively. The presence of the water molecule causes the displacement of the terminal methyl group resulting in less interdigitation than is found in the anhydrous \( n \)-alkylammonium chlorides.

This structure further extends the relevance of \( n \)-alkylammonium halides as models for biomembranes, and the effect of surrounding water molecules on membranes.
*n*-Dodecylammonium chloride (C_{12}H_{25}NH_{3}Cl)

The cell dimensions were first determined by using a moving film variable-temperature powder camera [Gordon, 1953]: monoclinic, \(a=5.68 \text{ Å}, \ b=7.16 \text{ Å}, \ c=17.86 \text{ Å}, \ \beta=91.2^\circ, \ d(001)=17.86, \ Z=2\) with two possible space groups given as \(P2_1/m\) and \(P2_1\).

The structure was redetermined from single crystals grown from ethanol [Silver and Marsh, 1995]. Hydrogen atoms were refined in the determination, resulting in a reliable structure with \(R=0.035\).

![Fig 7.5: Packing of *n*-dodecylammonium chloride ethanol [Silver and Marsh, 1995].](image)

**Single crystal data:**

Monoclinic

\[
\begin{align*}
\text{a} &= 5.682 \text{ Å}, \ b = 7.186 \text{Å}, \ c = 17.775 \text{Å} \\
\beta &= 92.75^\circ \\
Z &= 2 \\
\text{Space group} &= P2_1
\end{align*}
\]

The average distance between alternating carbons was found to be 2.51 Å.

*n*-Alkylammonium bromides:

The structure of only one interdigitated *n*-alkylammonium bromide has been reported
in the literature - that of n-dodecylammonium bromide (C$_{12}$H$_{23}$NH$_3$Br) [Lunden, 1974].

A powder diffraction camera was employed to determine cell dimensions and possible space group [Gordon et al, 1953]. The photographs proved the packing to be Monoclinic

\[ \begin{align*}
    a &= 6.06 \text{Å}, \\
    b &= 7.02 \text{Å}, \\
    c &= 35.8 \text{Å}, \\
    \beta &= 91.6^\circ
\end{align*} \]

\[ d(001)=35.8 \]

\[ Z=4 \]

Space group \( P2_1/c \)

Approximate fractional co-ordinates projected on the \( ac \) plane were determined.

A single crystal study was undertaken to determine the three dimensional structure from crystals isolated from acetone [Lunden, 1974].

Fig 7.6: Packing of n-dodecylammonium bromide [Lunden, 1974].

*Single crystal data:*

Monoclinic

\[ \begin{align*}
    a &= 6.030 \text{Å}, \\
    b &= 6.958 \text{Å}, \\
    c &= 35.639 \text{Å} \\
    \beta &= 92.09^\circ
\end{align*} \]

\[ Z=4 \]

Space group \( P2_1/c \)

The alkyl chains pack in an orthorhombic subcell with \( a_s=6.96, b_s=5.40 \) and \( c_s=2.54 \). This packing is similar to \( O'\perp \).
Structures that are related to interdigitated $n$-alkylammonium halides are those of the perovskite-type layered compounds $(C_{n}H_{2n+1} \text{NH}_{3})M\text{Cl}_{4}$. These types of compounds also act as models for biomembranes. The layers consist of corner sharing $\text{Cl}_{6}$ octahedra with a metal ion in their centres. Different structures and chain packings are observed depending on the number of carbon atoms in the chain and the metal ion. Interdigitated structures were observed for $M=$Co and $M=$Zn. Fig 7.7 shows the structure for $M=$Zn, $n=13$.

![Diagram of interdigitated packing](image)

**Fig 7.7:** Interdigitated packing of perovskite-type layered compounds [Zuniga and Chapuis, 1983]

### 7.2.2 Non-interdigitated phase

![Diagram of non-interdigitated phase](image)

**Fig 7.8:** Non-interdigitated phases of $n$-decylammonium chloride [Schenk, 1989]

It was observed [Libscomb and King, 1950] that $n$-alkylammonium halides crystallised below the temperature of their first solid state transition exhibit monoclinic or orthorhombic symmetry. Gilson [1976] revealed a discontinuity in the long spacings of $n$-alkylammonium halides when going from 16 to 17 carbons in the $n$-alkylammonium chain. This reveals the change from a preferred interdigitated
structure to a non-interdigitated structure when crystallisation occurs at room temperature — C\textsubscript{16}Cl is interdigitated, and C\textsubscript{17}Cl non-interdigitated. It is however still possible to obtain the interdigitated phase of C\textsubscript{17}Cl to C\textsubscript{19}Cl by choosing the right crystallisation conditions — by lowering the temperature of crystallisation the more stable interdigitated phase will form.

One structure that has been determined as non-interdigitated from crystallisation at room temperature is that of \textit{n}-octadecylammonium chloride [Scholtz, 1997]. The chains pack in V-shaped dimers.

\textit{Single crystal data:}

\textit{Orthorhombic}

\begin{align*}
a &= 5.3693 \text{ Å} , \\
b &= 70.905 \text{ Å} , \\
c &= 5.4505 \text{ Å} \\
Z &= 4 \\
\text{Space group} & \ P2_1nb \\
R &= 0.1505
\end{align*}

Unlike the room-temperature phases of \textit{n}-alkylammonium chlorides with \textit{n}< 16, which is interdigitated with chains in the \textit{trans} conformation, this structure is non-interdigitated, and the molecule packs with a kink between the second and third carbon atoms. The kink in the molecule prevents the molecules to interdigitate, because the effective chain diameter is too large.

![Fig. 7.9: A molecule of \textit{n}-octadecylammonium chloride indicating the kink between carbons 2 and 3](image-url)
The factors influencing the formation of an interdigitated or non-interdigitated structure has been described by Kind et al. [1982]. If the chains are approximated as cylinders with an effective diameter $D$, it is clear that $D$ will increase with increasing temperature as the chains start to rotate and defects such as kinks become present. This increase in disorder can be described as an average nematic order parameter $S$, thus $D$ is a function of $S$: $D = D(S)$. To simplify the situation, it is assumed that the ends of the chains are attached to a square lattice with dimension $a$. If $a$ is smaller than $2D$, the only packing possible is non-interdigitated. The optimum packing will be obtained if the molecule is tilted:

$$\cos \theta_1 = \frac{D}{a} \quad (a < 2D)$$

where $\theta_1$ is the angle formed by the average chain axis and the normal to the layers.

If however, $a > 2D$, then both the interdigitated and non-interdigitated structures are possible. With the interdigitated structure the optimum packing is obtained with a smaller tilt angle $\theta_2$

$$\cos \theta_2 = \frac{2D}{a} \quad (a > 2D)$$
Fig 7.11: Diameter of chains relative to $a$

With increasing temperature, the diameter of the chain increases, making $a < 2D$, and the most stable possible structure changes form a interdigitated to a non-interdigitated packing of molecules. A question that could be asked is why the kink is formed between the second and the third carbon atoms. Clearly the determining factor of increasing temperature means increasing diameter, but why not a kink at any other place in the chain?

The author speculated that the kink is the result of two extra hydrogen bonds formed between the first carbon atom and the chlorine. In previously determined structures such as $n$-decylammonium chloride [Schenk and Chapuis, 1986] and $n$-dodecylammonium chloride [Silver and Marsh, 1995], the chlorine forms only three hydrogen bonds to the ammonium group, and no hydrogen bonds to any of the carbon atoms. These extra hydrogen bonds can thus stabilise the disordered molecule — “cancelling out” the disorder and pinning the kink down. It can also be speculated that the ionic interaction between the ammonium ions is stronger than the van der Waals interaction between the carbon parts of the chains and that a network of hydrogen bonding between the ionic layers is formed first.
A structure related to the non-interdigitated structure of \( n \)-octadecylammonium chloride is that of di-\( n \)-octadecylammonium bromide. [Nyburg, 1996]

**Fig 7.12:** Molecule of di-\( n \)-octadecylammonium chloride [Nyburg, 1996].

**Single crystal data:**
\[ a = 5.392 \text{ Å} \]
\[ b = 67.18 \text{ Å} \]
\[ c = 5.374 \text{ Å} \]
\[ Z = 2 \]
Space group \( P2_12_12_1 \)

**Fig 7.13:** Packing of molecules of di-\( n \)-octadecylammonium chloride in V-shaped dimers [Nyburg, 1996].
Crystals were grown at 15° C by slow evaporation from a toluene/chloroform solution. The diffraction data was of rather poor quality, and several problems had to be solved before the structure could be refined. According to the author, this structure determination could not be expected to give accurate atomic co-ordinates.

The molecules form dimers that also exhibit V-shaped packing. The N atom and the first three C atoms form a coplanar zig-zag, and there is a kink between the third and the fourth carbon atoms in the chain. The author speculates that the kink is due to the presence of the bulky bromide ion lying close to the N atom, which is clearly not the case because n-octadecylammonium chloride with the smaller chloride ion also exhibits a kink in the chain. This is the first structure of a secondary n-alkylammonium halide that has been determined, and no literature about the existence of different polymorphs of these compounds is available. It is may be possible to form an interdigitated structure at lower temperatures if the effective chain diameter decreases. It will proof interesting to investigate the structure of the compound crystallised at lower temperatures to determine the possibility of polymorphism.

It was found that certain C-C bond lengths were longer than the expected 1.51 Å. The C2-C3 bond was 1.59 Å, and the C3-C4 1.66 Å. The author speculates that this discrepancy is due to conflict between the hydrogen atoms on Cl and C4. The distance between H1A and H4B is only 2.21 Å, compared to the distance of 2.4 Å normally found. It is interesting to note that we also detected a discrepancy in the C-C bond lengths of n-octadecylammonium bromide (See experimental section).

Structures that are related to non-interdigitated n-alkylammonium halides are those of some perovskite-type layered compounds (C_{10}H_{21}NH_{3})MCl_{4} [Zuniga and Chapuis, 1983]. Two non-interdigitated structures will be discussed briefly.
The low temperature structure of (C\textsubscript{10}H\textsubscript{21}NH\textsubscript{3})CdCl\textsubscript{4} has been determined [Blinc \textit{et al}, 1979; Kind \textit{et al}, 1979; Ricard \textit{et al}, 1984; Casal \textit{et al}, 1985].

![Fig 7.14: Packing of (C\textsubscript{10}H\textsubscript{21}NH\textsubscript{3})CdCl\textsubscript{4} [Blinc \textit{et al}, 1979]](image)

The structure consists of layers of \textit{n}-alkylammonium chains and CdCl\textsubscript{4} layers, tilted 40° relative to the normal of the layer. The ammonium ions form hydrogen bonds with the chloride ions, and each chain is co-ordinated with six others. A dimer is formed, packing in a V-shaped pattern. This compound exhibits two solid state phase transitions at 35° C and 39° C [Kind \textit{et al}, 1979]. These phase transitions have been studied extensively via NMR, calorimetric, X-ray diffraction and vibrational spectroscopic techniques [Blinc \textit{et al}, 1979]. The space group of the low temperature phase is \textit{P2\textsubscript{1}/n} and transforms into the intermediate temperature phase (\textit{Pmnn}). This phase transforms to the high temperature phase (\textit{Amma}).

The low temperature phase is monoclinic, with two different chains (A and B) present in the structure. For the A chain the kink is located between the first and second carbon atom, and for the B chain between the second and third carbon atom.

The structure of (C\textsubscript{10}H\textsubscript{21}NH\textsubscript{3})CuCl\textsubscript{4} [Kozelj \textit{et al}, 1981] exhibits a different molecular packing.
Fig 7.15: Packing of $(\text C_{10}\text H_{21}\text NH_3)\text Cu\text Cl_4$ [Kozelj et al, 1981]

The dimer formed is not V-shaped, instead the alkyl chains point to opposite directions. The chains are parallel and tilted $40^\circ$ relative to the normal of the layers.
7.2.3 High temperature structures

Busico et al [1983] found that n-alkylammonium halides exhibit three step melting behaviour – the low temperature phase firstly transforms to a plastic phase by conformational disordering of the hydrocarbon chains. In this phase the chains are held together by the ionic forces of the end groups. The plastic phase transforms to a mesomorphic liquid (a smectic mesophase), which in turn melts to form a clear liquid still containing a certain degree of ordering, and resembling a less organised smectic mesophase [Tsau and Gilson, 1968].

An X-ray photograph study [Busico et al, 1983] indicated tetragonal symmetry for the plastic phase. A halo on the photograph commonly found in molten normal hydrocarbons indicated the conformational disorder of the carbon chains. X-ray photographs of the mesomorphic liquid exhibited one sharp reflection (001) and a diffuse halo indicative of a smectic phase. The long spacings in the mesomorphic liquid, named by the authors as smectic I, were found to be lower than the long spacings of the plastic phase. The clear liquid phase was found not to be isotropic - the (001) reflection was still present, but it was broader than in both the plastic and the mesomorphic liquid phase. The clear liquid phase was named smectic II.

Fig. 7.16. Long spacings versus no of carbons in alkyl chain of n-alkylammonium chlorides

The long spacings in the mesomorphic liquid, named by the authors as smectic I, were found to be lower than the long spacings of the plastic phase. The clear liquid phase was found not to be isotropic - the (001) reflection was still present, but it was broader than in both the plastic and the mesomorphic liquid phase. The clear liquid phase was named smectic II.
DSC investigations

Tsau and Gilson [1968] investigated the polymorphism of normal alkylammonium halides by means of DSC. Transition temperatures and enthalpies were measured for \( n \)-alkylammonium chlorides and bromides with carbon chains ranging from C\(_1\) to C\(_{16}\). For the chloride series two transitions were found for C\(_1\), C\(_3\) — 8 and C\(_{10}\) and three transitions for C\(_n\), n=9 and 10<n<17. For the bromide series two transitions were observed for C\(_1\), C\(_3\), C\(_4\), C\(_{10}\) - C\(_{16}\) and three transitions for n=7 and n=9.

It was observed that for the transitions occurring at the lowest temperature the transition temperature alternated with odd or even number carbon in the series (Fig. 7.17 and Fig. 7.18 )

![Transition temperatures](image)

Fig. 7.17: Temperatures of phase transitions of \( n \)-alkylammonium bromides
Fig. 7.18: Temperatures of phase transitions of $n$-alkylammonium chlorides

The melting temperature however, increased linearly with increasing number of carbons in the chain. It can thus be expected that melting occurs from a similar structure in all members of the series. Certain $n$-alkylammonium halides exhibited a change in the DSC profile if the sample was scanned more than once. This indicates the "freezing in" of disorder upon solidification, and the formation of a metastable phase. For $\text{C}_1\text{Cl}$, $\text{C}_8\text{Br}$ and $\text{C}_{14}\text{Br}$ the sample returned to the original state after a month, but for $\text{C}_{12}\text{Cl}$, $\text{C}_{16}\text{Cl}$ and $\text{C}_9\text{Br}$ the samples did not revert to the original structure even after two months of storing.

The thermal phase transitions of $n$-decanlammonium chloride ($\text{C}_{10}\text{H}_{21}\text{NH}_3\text{Cl}$) have been investigated extensively [Kind et al, 1982; Seliger, 1983; Schenk et al, 1989; Reynhardt et al, 1992]. Five solid phases of this compound have been identified and investigated.

Fig 7.19 indicates the phase transitions with increasing temperature.
Crystallisation by slow evaporation at room temperature yields the interdigitated, monoclinic low temperature polymorph. This phase transforms to an non-interdigitated, orthorhombic, $\delta$ phase at $39^\circ$C. All the high temperature phases are non-interdigitated. At a higher temperature ($41^\circ$ C) the $\delta$ phase transforms to the orthorhombic $\beta$ phase, that in turns transforms to the high temperature $\alpha$ phase at $43^\circ$C before melting. Cooling of the melt cause the same sequence of phases with decreasing temperatures, except that the $\delta$ phase does not transform to the initial monoclinic interdigitated phase. Instead a metastable non-interdigitated, triclinic $\varepsilon$
phase is formed from the $\delta$ phase. On further cooling this metastable $\varepsilon$ phase slowly transforms to the more stable interdigitated state. However, a fully interdigitated phase is never reached.

Various analytical techniques have been employed to shed light on the structure of the higher temperature phases of $n$-decylammonium chloride. These include DSC \cite{Reynhardt et al, 1992}, X-ray powder diffraction \cite{Reynhardt et al, 1992; Seliger et al, 1983}, NMR \cite{Reynhardt et al, 1992}, electrical conductivity \cite{Shigehiko et al, 1993} and vibrational spectroscopy \cite{Schenk et al, 1989}.

It has been observed \cite{Schenk et al, 1989} that conformational defects are present in all the high temperature phases $\delta$, $\beta$ and $\alpha$, as well as in the metastable $\varepsilon$ phase. The concentration of defects increases with increasing temperature. In the $\delta$, $\alpha$ and $\beta$ phases the molecules can be viewed as cylinders due to the presence of the defects.

The $\delta$ phase is monoclinic and non-interdigitated, resulting in a linear hydrogen bond pattern. The chains are fully extended, resembling the structure of the non-interdigitated polymorph of $n$-octadecylammonium chloride. However, in the case of $n$-decylammonium chloride the chains constituting the dimers are parallel and not V-shaped as determined for $n$-octadecylammonium chloride.

The structure of the $\varepsilon$ phase is similar to that of the $\delta$ except that the hydrogen bond network is distorted.

The structure of the $\alpha$ phase may be described by a "tree" model \cite{Schenk et al, 1989}. A rigid square lattice is formed by the chlorine atoms, with the chlorine atoms forming a square pyramidal cavity. The polar end of the $n$-alkylammonium chain fits into this cavity. The packing in this phase is not tight, with an approximate area of 25 $\text{Å}^2$ per chain.
The $\beta$ phase is stable only in a narrow temperature range of approximately $2^\circ$C. The structure determination is hampered as reflections of the neighbouring phases are also present. It was speculated [Schenk et al, 1989] that the $a$ and/or $b$ lattice parameters are intermediate between the ones of the $\alpha$ and $\delta$ phases.

Reynhardt et al [1992] investigated these transitions by means of DSC. An example of a DSC scan is shown in Fig.7.21. It must be noted that subsequent scans differed in shape, when the sample was scanned more than once.

Because the thermal behaviour of $n$-decylammonium chloride has been investigated extensively, it can be considered as a model for the phase behavior of other $n$-alkylammonium halides. In this investigation the assumption is
made that $n$-alkylammonium chlorides and bromides with 18 carbons in the molecules exhibit the same phase transitions as $n$-decylammonium chloride.

7.3 Conclusion

Not many structures of $n$-alkylammonium halides with the number of carbon atoms in the range 10 to 20 have been reported in the literature. Furthermore, the reported structures are mostly of the most stable, interdigitated phase. It is evident that before structure determination by extrapolation from known structures can be performed, more "key" structures must be determined. The isostructurality of the same polymorphic forms with a different number of carbon atoms is clear from the change in long spacing with the number of carbon atoms.

No reports were found in the literature on the structures of $n$-alkylammonium iodides. It would be interesting to investigate the effect of a larger ion on the packing of the molecules. We therefore focussed our experimental work on obtaining the structures of $n$-alkylammonium halides with 18 carbon atoms in the chain, but with different anions and different polymorphs of the same compound. This subject will be discussed further in the experimental section.
Chapter 8

Esters

Long-chain esters are the major components of many waxes. The structural behavior of esters will influence the structure of waxes to a great extent. These moieties can act as bridging molecules between lamella, reducing the intensities of the lamellar reflections, and possibly leading to a less crystalline structure.

8.1 Methyl esters

Evidence was given [Malkin, 1931], that methyl esters crystallize as dimers. From the measurement of long spacings, it was assumed that methyl esters exhibit two polymorphic forms, depending on the parity of the number of carbon atoms, and the temperature. Methyl esters of acids with an odd number of carbon atoms, i.e. CH₃O(CH₂)ₙCH₃, exhibit two polymorphic forms, one stable at ambient temperatures, and one near the melting point. It was incorrectly assumed that methyl esters of even fatty acids exhibit only one polymorphic form.

![Diagram of long spacing of methyl esters](image-url)

**Fig 8.1:** Change of long spacings of methyl esters with the number of carbon atoms in the molecule.
The long spacings of melted samples were measured [Malkin, 1931] a few degrees below the melting point. When a melted sample was allowed to cool to room temperature, the long spacing changed to the value of the long spacing of the pressed sample. It was stated that for the methyl esters with an odd number of carbon atoms, the long spacings from the pressed sample and the melted sample are equal — this indicates that only one crystal structure is present at all temperatures. However, for methyl esters with an even number of carbon atoms, a transformation occurs to a metastable polymorph near the melting point. From the long spacings it can be concluded that, in the case of the pressed sample, layers are formed by dimers tilted at angles of 63.0° and 67.5° for the odd and even esters respectively. For esters with an even number of carbon atoms, the metastable polymorph that exist near the melting point consists of lamella formed only by single molecules tilted 75° relative to the surface of the terminal methyl groups.

Evidence was given from melting point and crystal spacing (d(001)) determinations [Francis and Piper, 1939] that, contrary to reports by Malkin [1931], the methyl esters with an odd number of carbon atoms also transforms to a new modification just below melting point.

The crystal structure of the monoclinic polymorph of methyl octadecanoate (methyl stearate) was determined by means of rotation and Weissenberg X-ray photographs at room temperature [Aleby and von Sydow, 1960].

**Single crystal data:**

- $a = 5.61 \pm 0.02$ Å
- $b = 7.33 \pm 0.02$ Å
- $c = 106.6 \pm 0.6$ Å
- $\beta = 116.78 \pm 0.3^\circ$
- $Z = 8$
- $d (001) = 95.2 \pm 0.3$ Å

Space group A2/a
Fig. 8.2: Packing of methyl octadecanoate [Aleby and von Sydow, 1960].

The molecules crystallize as dimers, with O⊥ packing of the hydrocarbon chain. It was speculated that the molecules crystallize as dimers as a result of polar forces interacting between the O and C atoms.

The existence of an orthorhombic polymorph of methyl octadecanoate [MacGillavry and Wolthuis-Spuy, 1970] indicated the presence of polymorphism. Crystals of the orthorhombic form of methyl octadecanoate was grown at reduced temperatures (-12° C to -15°C). The structure was determined from X-ray rotation and Weissenberg photographs [MacGillavry and Wolthuis-Spuy, 1970].

**Single crystal data:**

\[ a = 5.613 \pm 0.005 \, \text{Å} \]

\[ b = 7.354 \pm 0.005 \, \text{Å} \]
$c = 95.147 \pm 0.004 \text{ Å}$

$Z = 8$

Space group: \textit{Pnab}

\textbf{Fig 8.3:} Orthorhombic modification of methyl octadecanoate: projection on the \textit{bc}-plane [MacGillavry and Wolthuis-Spuy, 1970].

\textbf{Fig 8.4:} Orthorhombic modification of methyl octadecanoate: Projection on the \textit{ac}-plane. [MacGillavry and Wolthuis-Spuy, 1970].

The crystal structures of the monoclinic and orthorhombic forms of methyl octadecanoate resemble each other when projected on the \textit{bc} plane. The \textit{a} and \textit{b} unit cell dimensions are very similar. However, when projected on the \textit{ac} plane, the difference is clearly visible. The orthorhombic form also crystallizes in dimers, but consecutive dimers form V-shaped pattern, unlike the parallel packing of molecules in the monoclinic form. This is a result of the difference in tilt angles between two consecutive dimers. In this article
reference was made to the observation of another monoclinic form obtained from the melt, but the authors did not report the structure.

A thermal study of the methyl and ethyl esters of octadecanoic acid was conducted by Sullivan [1973]. Two different crystallization methods were used – crystallization from the melt and from solution. The melting range for the sample obtained from the melt was lower than that crystallized from solution. No phase transitions before the melting point was observed for either the melt crystallized or the solution crystallized sample. The author speculates that the instrumentation was not sensitive enough to resolve the transitions before melting point.

8.2 Ethyl esters

As early as 1931 it was found [Malkin] that ethyl esters exhibit two different polymorphs – one stable at room temperature, and one stable within a narrow temperature range below the melting point. In contrast with the dimers formed by methyl esters, ethyl esters crystallize in lamella consisting of single molecules.

Long spacings of ethyl esters were determined using two different methods of sample preparation:

i) solvent crystallized material pressed on a glass slide

ii) material melted on a glass plate
Fig 8.5: Change of long spacing of ethyl esters with number of carbon atoms in the ester [Malkin, 1931].

In a plot of long spacings against the number of carbon atoms in the ethyl esters, two lines are evident (Fig 8.5). This indicates two isostructural series, or polymorphic modifications. The long spacing of the melted sample was determined a few degrees below the melting point for every ethyl ester. It must be noted that if the melted sample was allowed to cool to room temperature the long spacings changed to that of the pressed sample, similar to the behavior of methyl esters. The author proposed that the difference in long spacings of the polymorphs is due to a change in the tilt of the chain relative to the surface of the methyl end groups. In the one form, called the $\beta$-form, the chains are tilted 67.5° relative to the terminal methyl plane. The form that crystallizes just below melting point is called the $\alpha$-form, and contains vertical chains. At lower temperatures the $\alpha$-form undergoes a transition to the $\beta$-form. In the $\beta$-form, the chains are tilted 67.5° relative to the terminal methyl plane.

Methyl esters melt at higher temperatures than ethyl esters. This is probably due to the fact that ethyl esters crystallize with one molecule in the layer, and methyl esters crystallize as dimers, resulting in stronger forces keeping the molecules together.
The crystal structure of ethyl octadecanoate (ethyl stearate) was reported in 1962 [Aleby]. Crystals were obtained from a sample crystallized by solvent evaporation at room temperature, and the projections of the molecules on the $ac$ and $bc$ planes were determined from X-ray rotation and Weissenberg photographs.

**Fig. 8.6:** Packing of ethyl octadecanoate [Aleby, 1962].

**Single crystal data:**
- $a = 5.59 \pm 0.02$ Å
- $b = 7.40 \pm 0.02$ Å
- $c = 57.1 \pm 0.40$ Å
- $\beta = 118.5^\circ$
- $Z = 4$
- Space group: $Aa$

The $a$ and $b$ values are similar to those found for methyl octadecanoate, but the layers contain only one molecule, resulting in a smaller $c$ unit cell dimension. The molecule was presumed to have a kink at the ester group.
This conformation of the ester group, however, was proven to be incorrect [Mathieson and Welsh, 1965]. The authors stated that the C-O-C and O-C-C angles of 138° and 140°, as well as the trans position of the alcohol α-carbon relative to the C=O group reported by Aleby [1962] were questionable. Usually these angles are in the range of 108 – 115°, and the α-carbon is cis to the C=O group. The conformation of the functional group was redetermined from X-ray photographs, and proven not to have a kink, and with a cis ester group. The space group was shown to be Ia, opposed to the space group Aa as reported by Aleby. From photographic projection techniques, it would not be possible to distinguish between these two space groups.

Fig 8.7: Conformation reported by Aleby [1962] (left), corrected by Mathieson and Welsh [1965] (right).

To further prove their statement, the authors determined the structure of ethyl behenate (C_{2}H_{5}OOC_{22}H_{43}) by means of X-ray photographic methods.

**Single crystal data:**

\[ a = 5.54 \, \text{Å} \]
\[ b = 7.43 \, \text{Å} \]
\[ c = 67.0 \, \text{Å} \]
\[ β = 118° \]

Space group: Ia
Sullivan [1973] indicated that the temperature and thermal history influence an ethyl esters' thermal behavior. If a sample crystallized from the melt was cooled below 298 K, two solid-solid phase transitions became apparent. The form crystallized from the melt transformed to the more stable form that is obtained from solution with time. The rate of transformation was proved to be a function of temperature – the higher the temperature, the faster the transformation. Low angle X-ray diffraction indicated that the form that crystallizes from solution is the monoclinic form, as described by Aleby [1962].

8.3 Propyl esters

Propyl esters exhibit two crystalline forms, the high temperature α-form, and the β-form at lower temperatures. The structure of crystals grown at room temperature were determined from X-ray photographs [Aleby, 1968]. The xz projection was however extrapolated from the structure of ethyl stearate, determined erroneously by Aleby [1962] - as indicated before, the conformation of the ester group was not correct. The author stated that the atoms in the propoxy group had very high B values, indicating the uncertainty in their positions. When the propoxy chain was changed to resemble a normal carboxyl group, the structure improved.

Fig 8.8: Projection of propyl octadecanoate on ac-plane
**Single crystal data:**

Monoclinic

\[ a = 5.59 \pm 0.02 \, \text{Å} \]

\[ b = 7.39 \pm 0.02 \, \text{Å} \]

\[ c = 3.00 \pm 0.3 \, \text{Å} \]

\[ \beta = 119.2 \pm 0.3^\circ \]

\[ Z = 2 \]

Space group: \( Pa \)

The molecules are arranged in layers with parallel chain axes, with the hydrocarbon packing O.L. No indication was given whether the molecules pack as dimers or not. Pertaining the small value of the \( c \) unit cell axis, the lamella are most likely formed by single molecules.

**8.4 Symmetrical esters**

Symmetrical esters are formed by the esterification of fatty acids and fatty alcohols containing the same number of carbon atoms in the chain. Kohlhaas [1938; 1940] determined the unit cell dimensions of hexadecyl hexadecanoate, \( C_{15}H_{31}COOC_{16}H_{33} \) (cetyl palmitate), by means of X-ray photographs.

**Single crystal data:**

Monoclinic

\[ a = 5.61 \, \text{Å} \pm 0.5\% \]

\[ b = 7.415 \, \text{Å} \pm 0.2\% \]

\[ c = 77.90 \, \text{Å} \]

\[ \beta = 61.30^\circ \pm 0.8\% \]

Space group \( P2_1/c \)

These cell dimensions were redetermined by electron diffraction experiments [Dorset, 1976]. Another polymorphic form was proved to exist: the major monoclinic form
described by Kohlhaas, and a less-favoured orthorhombic polymorph. The polymorph obtained from crystallization is influenced by the polarity of the solvent – the monoclinic form is obtained from both polar and non-polar solvents, and the orthorhombic form only from non-polar solvents, together with the monoclinic form.

Unit cell dimensions determined by Dorset for the monoclinic form agree well with those of Kohlhaas:

**Single crystal data:**

\[
\begin{align*}
a &= 5.59 \pm 0.08 \text{ Å} \\
b &= 7.46 \pm 0.03 \text{ Å} \\
c &= 79.4 \text{ Å}
\end{align*}
\]

The author expressed uncertainty about the space group previously reported. Even though Kohlhaas determined the space group as \(P2_1/c\) from observed systematic absences, other similar aliphatic compounds exhibit the space group \(P2_1/a\). This spacegroup is also favored by Dorset.

The chains are tilted 60° relative to the lamellar planes, and the subcell of the hydrocarbon chains is O\(_\perp\). The oxygen of the ester group is expected not to differ much from a carbon atom, causing the molecule to resemble a normal alkane chain with 33 carbon atoms. The packing is expected to be similar to that of an odd numbered paraffin, but this is not the case – the molecules pack in a way comparable to an even numbered monoclinic paraffin.

The orthorhombic polymorph of hexadecyl hexadecanoate also exhibits the O\(_\perp\) subcell, similar to odd \(n\)-alkanes, with

\[
\begin{align*}
a &= 7.45 \pm 0.16 \text{ Å} \\
b &= 4.97 \pm 0.01 \text{ Å}
\end{align*}
\]

and plane group \(pgg\).
The chains are packed normal to the 001 face of the crystal, but no three dimensional crystal structure determinations have been performed. It would be interesting to see the exact packing of molecules in the structure, in order to determine the forces directing the packing.

Molecular orientation and packing of films of esters on a substrate were investigated by Sutula and Bartell [1961] by means of electron diffraction. The films consisted of crystallites with their 001 plane parallel to the surface of a platinum substrate.

The following unit cell dimensions were determined:

<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(b)</th>
<th>Space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octadecyl octadecanoate</td>
<td>5.56</td>
<td>7.53</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Hexadecyl octadecanoate</td>
<td>5.65</td>
<td>7.40</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Dodecyl dodecanoate</td>
<td>5.68</td>
<td>7.50</td>
<td>Monoclinic</td>
</tr>
</tbody>
</table>

8.5 Long chain unsymmetrical esters

Evidence was given [Zhang, 1989] that tetradecyl octadecanoate (myristyl stearate) crystallize in an orthorhombic form. The unit cell dimensions are

\[a = 7.63 \, \text{Å}\]
\[b = 4.98 \, \text{Å}\]
\[c = 87.8 \, \text{Å}\]

Space group: \(A2\text{I}am\)

8.6 Conclusion

From the presented literature it is clear that not many reliable structures have been determined for long-chain ester molecules. There is also much uncertainty about the thermal behavior of these molecules, especially because some of the esters investigated in the earlier years may contain other esters as impurities that may influence the thermal behavior as well as the polymorphism of the compound. It is clear that more structures
should be solved before a general trend may be recognized in the packing and crystallographic characteristics of long chain esters.
Section B

Experimental work
The structures and thermal behavior of the methyl, ethyl and propyl esters of \(n\)-octadecanoic acid have been studied by various researchers [Aleby, 1962; Mathieson and Welsh, 1965; Aleby, 1968; MacGillavry and Wolthuis-Spuy, 1970]. We were interested in the packing of methyl and ethyl esters of the acid with one less carbon atom, namely the esters of \(n\)-heptadecanoic acid. Comparison of the structures of esters of odd and even fatty acids will facilitate the understanding of the factors directing the packing.

9.1 Methyl- and Ethyl heptadecanoate

9.1.1 Synthesis:

Methyl heptadecanoate (\(n\)-CH\(_3\)OOC\(_{17}\)H\(_{35}\)) and ethyl heptadecanoate (\(n\)-C\(_2\)H\(_5\)OOC\(_{17}\)H\(_{35}\)) were prepared by reactions (1) and (2) respectively.

\[
\begin{align*}
\text{OH} + \text{CH}_3\text{OH} & \rightarrow \text{O}H + \text{CH}_3\text{O}\text{H} + \text{H}_2\text{O} \\
\text{OH} + \text{CH}_3\text{CH}_2\text{OH} & \rightarrow \text{O}H + \text{CH}_3\text{CH}_2\text{O}\text{H} + \text{H}_2\text{O}
\end{align*}
\]

(1)

(2)

Method:
The method was adapted from the synthesis of ethyl dodecanoate from ethanol and \(n\)-dodecanoic acid. It must be mentioned that no effort was made to optimize yield of the reactions by variation of reaction conditions. Generally the yield was in the range of 50 to 60%.

128
0.004 moles of the acid was treated with 20 ml alcohol in a round bottom flask. To this mixture was added 5 ml concentrated HCl as catalyst. A spatula of anhydrous calcium chloride was added to the reaction mixture to absorb the water. A reflux condenser was fitted to the flask, and the mixture was refluxed for 48 hours.

The flask was removed from the heat, and the reaction mixture allowed to cool. The mixture was extracted four times with 20 ml portions diethyl ether. After evaporation of the ether, the product was obtained. The ester was recrystallized from methanol, and purified by chromatography, using a flash silica column with a hexane/ethyl acetate solution in a 3:7 ratio as eluant. The final product was characterized by mass spectroscopy.

9.1.2 Crystallization and X-ray diffraction

Various attempts were made to obtain single crystals of the purified esters by means of solvent evaporation. Very small, plate shaped crystals of ethyl heptadecanoate were obtained from different solvents, but the crystals were too thin to detect the diffracted X-rays. A more serious problem was encountered with methyl heptadecanoate: due to the low melting point of the substance (32.2°C) the ester undergoes a phase transition if it is attempted to cut the crystal under the polarized microscope. The crystals completely lose their shape if cut, implicating a force induced phase transition. These problems may be overcome if sample preparation and data collection are performed at reduced temperatures. This behavior, however, led to an interest in the thermal behavior of the compound.
9.1.3 Thermal measurements

Thermal investigations were performed by employing differential scanning calorimetry (DSC). Two instruments were used for data collection.

1.) A Thermal Analysis 5000 instrument at the laboratory of Reckitt and Coleman, Johannesburg.
2.) A Perkin Elmer instrument at the Chemistry Department of Rhodes University, Grahamstown.

No significant progress was made in determining the structure of the methyl and ethyl esters of \( n \)-heptadecanoic acid. However, the thermal behavior of methyl heptadecanoate was investigated by means of DSC. In Fig 9.1 a DSC scan of methyl heptadecanoate crystallized from carbon disulfide is shown. The sample was heated from -5°C at a rate of 5°C per minute, up to 40°C, and cooled down at the same rate to -5°C. On heating, only a single, melting endotherm (endotherm down) is observed at 32.22°C. However, on cooling two exothermic peaks are observed, one at 25.6°C and one at 20.86°C. The areas beneath the melting and crystallization peaks agree to approximately 92%.
Fig 9.1: DSC scan of methyl heptadecanoate
Fig 9.2: DSC scan of second heating run of methyl heptadecanoate.
**Fig 9.3:** Consecutive DSC scans of a sample of methyl heptadecanoate
The first DSC shows only one endotherm (endotherm up) on heating. In the second DSC run (Fig 9.2), however, two endotherms are present. The exothermic peaks obtained from the cooling run is similar to the exothermic peaks of the first DSC run. In Fig 9.3 a cyclic run is shown for the same sample used to obtain the second heating run. This same scan is shown in Fig 9.4 as a function of temperature. As can be seen in Fig 9.3 and Fig 9.4, the first, small endothermic peak is not well resolved in the first run, but increase in size with the second run. The second and third runs in Fig 9.3 superimpose perfectly, as can be seen in Fig 9.4. The first two melting endotherm in Fig. 9.3 represents solid-solid phase changes of form crystallized from solution. The second heating run is that of a sample crystallized from the melt. The difference in areas of the first and the second heating runs may indicate a difference in structure of the forms obtained from solution and from the melt.
9.2 Hexadecyl heptadecanoate and Heptadecyl heptadecanoate

9.2.1 Synthesis

These long chain esters were prepared by the following reactions:

**Hexadecyl hexadecanoate:**

\[
6 \text{C}_{16} \text{H}_{33} \text{OH} + 2 \text{Na}_2 \text{Cr}_2 \text{O}_7 + 8 \text{H}_2 \text{SO}_4 \rightarrow 3 \text{C}_{15} \text{H}_{31} \text{CO}_2 \text{C}_{16} \text{H}_{33} + 2 \text{Cr}_2(\text{SO}_4)_3 + 2 \text{Na}_2 \text{SO}_4 + 14 \text{H}_2 \text{O}
\]

**Heptadecyl heptadecanoate:**

\[
6 \text{C}_{17} \text{H}_{35} \text{OH} + 2 \text{Na}_2 \text{Cr}_2 \text{O}_7 + 8 \text{H}_2 \text{SO}_4 \rightarrow 3 \text{C}_{16} \text{H}_{33} \text{CO}_2 \text{C}_{17} \text{H}_{35} + 2 \text{Cr}_2(\text{SO}_4)_3 + 2 \text{Na}_2 \text{SO}_4 + 14 \text{H}_2 \text{O}
\]

**Method:**

To a cool solution of 10 ml concentrated \(\text{H}_2\text{SO}_4\) in 10 ml water in a 100 ml round bottomed flask, was added 0.008 moles of the alcohol. The mixture was stirred vigorously and placed in an ice bath. A solution of 0.002 moles of \(\text{Na}_2\text{Cr}_2\text{O}_7\) in 10 ml water was added dropwise to the mixture with stirring. The mixture was allowed to stir until the color changed from orange to green, indicating the change of oxidation state of \(\text{Cr}^{+6}\) to \(\text{Cr}^{+3}\). The mixture was extracted with four 30 ml portions of diethyl ether. The solvent was evaporated under reduced pressure, and the ester obtained. The product was further purified by chromatography on a flash silica column with a hexane/ethyl acetate 8:2 mixture as eluant. The ester was characterized by means of mass spectroscopy.

9.2.2 Crystallization

Attempts to obtain single crystals of the two esters were unsuccessful. The crystals were very thin and small, and barely visible under the polarizing microscope. It was decided to rather focus on X-ray powder diffraction as experimental technique, due to the difficulty in obtaining good quality single crystals.
9.2.3 X-ray powder diffraction studies

The powder diffraction pattern of a sample of the symmetrical ester heptadecyl heptadecanoate crystallized at room temperature was measured. Data were collected at room temperature on a Siemens D5000 X-ray powder diffractometer. A capillary sample holder was used to minimize preferred orientation. Monochromatic Cu Kα1 radiation was used to irradiate the sample, produced by the primary beam monochromator. Data was collected from 2.8° to 72° 2θ, with a stepsize of 0.01°, and measuring time of 60s per step.

Fig 9.5: Room temperature powder diffraction pattern of heptadecyl heptadecanoate.
The reflections were indexed using the indexing program Treor90 in the suite Crysfire.

The unit cell dimensions are:

**Orthorhombic**

\[ a = 4.5717 \text{ Å} \]
\[ b = 4.4810 \text{ Å} \]
\[ c = 41.2513 \text{ Å} \]

Calculated and experimental peak positions are compared in Table 9.1.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Heptadecyl Heptadecanoate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal system:</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Lattice Type:</td>
<td>P</td>
</tr>
<tr>
<td>Radiation:</td>
<td>Cu</td>
</tr>
<tr>
<td>WaveLength:</td>
<td>1.540598</td>
</tr>
<tr>
<td>Lattice Parameter:</td>
<td>( a = 41.2513 \text{ Å} ) ( b = 4.5717 \text{ Å} ) ( c = 4.481 \text{ Å} )</td>
</tr>
<tr>
<td>2Theta Start=</td>
<td>2.8</td>
</tr>
<tr>
<td>2Theta End=</td>
<td>50</td>
</tr>
<tr>
<td>Total 17 Experimental Peaks!</td>
<td></td>
</tr>
<tr>
<td>Total 16 matching Lines are found!</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>H</th>
<th>K</th>
<th>L</th>
<th>2Theta (Exp.)</th>
<th>2Theta (Calc.)</th>
<th>2Theta (Diff.)</th>
<th>d (Exp.)</th>
<th>d (Calc.)</th>
<th>Intensity (Exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>4.258</td>
<td>4.281</td>
<td>-0.022</td>
<td>20.73373</td>
<td>20.62564</td>
<td>1023.97</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>6.379</td>
<td>6.423</td>
<td>-0.044</td>
<td>13.84476</td>
<td>13.75043</td>
<td>2870.90</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
<td>10.678</td>
<td>10.715</td>
<td>-0.037</td>
<td>8.27873</td>
<td>8.25026</td>
<td>1105.33</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0</td>
<td>15.015</td>
<td>15.022</td>
<td>-0.007</td>
<td>5.89577</td>
<td>5.89304</td>
<td>887.42</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>19.942</td>
<td>19.915</td>
<td>0.028</td>
<td>4.44868</td>
<td>4.45479</td>
<td>1668.52</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>1</td>
<td>20.279</td>
<td>20.264</td>
<td>0.015</td>
<td>4.37561</td>
<td>4.37885</td>
<td>1948.47</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>1</td>
<td>20.870</td>
<td>20.833</td>
<td>0.037</td>
<td>4.25295</td>
<td>4.26048</td>
<td>3342.02</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>0</td>
<td>21.229</td>
<td>21.241</td>
<td>-0.012</td>
<td>4.18177</td>
<td>4.17944</td>
<td>2541.23</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>1</td>
<td>21.617</td>
<td>21.606</td>
<td>0.011</td>
<td>4.10764</td>
<td>4.10980</td>
<td>21105.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>23.940</td>
<td></td>
<td></td>
<td>3.71415</td>
<td></td>
<td>8606.22</td>
</tr>
<tr>
<td>14</td>
<td>0</td>
<td>1</td>
<td>36.442</td>
<td>36.466</td>
<td>-0.024</td>
<td>2.46349</td>
<td>2.46195</td>
<td>898.26</td>
</tr>
<tr>
<td>18</td>
<td>0</td>
<td>0</td>
<td>39.307</td>
<td>39.281</td>
<td>0.026</td>
<td>2.29031</td>
<td>2.29174</td>
<td>905.69</td>
</tr>
<tr>
<td>16</td>
<td>0</td>
<td>1</td>
<td>40.348</td>
<td>40.327</td>
<td>0.022</td>
<td>2.23356</td>
<td>2.23471</td>
<td>1189.22</td>
</tr>
<tr>
<td>19</td>
<td>0</td>
<td>0</td>
<td>41.579</td>
<td>41.562</td>
<td>0.018</td>
<td>2.17024</td>
<td>2.17112</td>
<td>944.43</td>
</tr>
<tr>
<td>17</td>
<td>0</td>
<td>1</td>
<td>42.311</td>
<td>42.324</td>
<td>-0.012</td>
<td>2.13436</td>
<td>2.13377</td>
<td>808.45</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>0</td>
<td>43.260</td>
<td>43.260</td>
<td>0.000</td>
<td>2.08971</td>
<td>2.08972</td>
<td>967.06</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>2</td>
<td>44.079</td>
<td>44.031</td>
<td>0.048</td>
<td>2.05277</td>
<td>2.05490</td>
<td>786.19</td>
</tr>
</tbody>
</table>

Table 9.1: Comparison of calculated and experimental peak positions.

One strong peak observed experimentally at 23.940° 2θ could not be indexed. All the other peaks could be indexed successfully. This peak may be due to the presence of an
impurity in the sample. Further attempts will be made in future work to index all the peaks in the diffraction pattern.
Chapter 10

*n-Octadecylammonium halides*

10.1 Synthesis

*n-Octadecylammonium* halide salts were prepared by dissolving *n*-octadecylamine in chloroform and adding the acid halide.

\[
\text{C}_{18}\text{H}_{33}\text{NH}_2 + \text{HX} \rightarrow \text{C}_{18}\text{H}_{33}\text{NH}^+ \text{X}^-
\]

The *n*-alkylammonium halide precipitate was filtered off. The product was characterised by mass spectrometry, and the purity checked by NMR spectroscopy.

In this manner *n*-octadecylammonium chloride, *n*-octadecylammonium bromide and *n*-octadecylammonium iodide was synthesised, using the acids HCl, HBr and HI.

To reveal the effect of an odd or even number of carbons in the molecule, it was attempted to synthesise *n*-heptadecylammonium halides using heptadecanol as starting material.

\[
p-\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Cl} + \text{CH}_3(\text{CH}_2)_{15}\text{CH}_2\text{OH} + \text{C}_5\text{H}_5\text{N} \rightarrow p-\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3 + \text{C}_5\text{H}_5\text{NH}^+\text{Cl}^-
\]

\[
p-\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3 = \text{C}_{17}\text{Tos}
\]
However, because this is a three-step reaction, and very low yields are obtained in each step, this synthesis was not viable. Another way to obtain heptadecylamine will be to use the acid as starting material. This synthesis was not investigated yet, but will be an interesting subject for future work.

10.2 Crystallization

As mentioned before, important factors determining the specific polymorph of a compound that crystallise include solvent, temperature of crystallisation and impurities present. The variable we adjusted was that of temperature (and in one example that of impurities.)

The compounds were crystallized by solvent evaporation employing different solvents and solvent systems. Solvents used include: methanol, ethanol, propanol, \( n \)-butane, \( n \)-heptane, chloroform, \( n \)-dodecane, 2,2,4- trimethylpentane, \( n \)-hexane, ethyl acetate, toluene, \( m \)-xylene and \( p \)-xylene. These single solvents were also expanded to binary and tertiary solvent systems. Varying the composition of the solvent may influence the rate of crystallisation and also the polymorphic composition obtained from crystallisation.

The method of vapour diffusion was also employed. Solvent \( S_1 \), containing the solute was prepared in a small container. This container was placed in a second larger, closed container that contained solvent \( S_2 \). Solvent \( S_2 \) was chosen so that, if it were mixed with solvent \( S_1 \), the solute would become less soluble in the mixture and crystallise. Diffusion of \( S_2 \) into \( S_1 \) (and \( S_1 \) into \( S_2 \)) should cause slow crystallisation of the solute.

Solvent diffusion entails the layering of solvents of different densities in the same container. The solute must be soluble in one of the layers, and less soluble in the other. This method may lead to crystallisation at the interface between the two layers.

In order to obtain different polymorphs, different crystallisation experiments were performed at different temperatures

1) room temperature
2) fridge (3°C)
3) freezer (-11°C)
To improve the quality of crystals, the solvent was allowed to evaporate at a very low rate, often taking a couple of months to evaporate.

Despite various efforts, single crystals of good quality were rarely obtained. Even when the crystal seemed to be useful under the polarising microscope, it was usually twinned (stacking twinning) due to the tendency of these compounds to crystallise in plates, stacked on top of each other, with the (001) plane as contact plane. Cutting such a twinned crystal would then cause the plates to shift relative to each other, resulting in broad peaks, split peaks, or shoulders on peaks. Several crystals were mounted and centred on the single crystal diffractometer, but the crystals were mostly not of good enough quality to even obtain lattice parameters.

Another factor that impairs the single crystal structure determination is the fact that for these long chain compounds one of the unit cell dimensions is long, causing diffraction peaks to lie very close to one another. Because Mo radiation was used in the single crystal diffraction data collection, these close peaks could not be resolved. A possible solution could be to rather use copper radiation, which should allow the peaks to become separate.

In order to determine the crystal structure of the low temperature (interdigitated) phase of n-octadecylammonium chloride, it was attempted to grow crystals of this compound at low temperatures (-13°C). Single crystals of good enough quality for structure determination could however not be obtained, and it was decided to focus on structure determination from powder diffraction data employing structure factor extraction, direct methods and Rietveld refinement.

Single crystals of n-octadecylammonium bromide and n-octadecylammonium iodide could be obtained. The single crystal structure of the first compound could be solved, but the diffraction data for the second compound were not of good enough quality to solve the structure.

We know from the literature that the structure of n-undecylammonium chloride hydrate was determined [Silver et al, 1996]. We tried to grow crystals of the hydrates of n-octadecylammonium chloride, -bromide, and -iodide by their technique, i.e. by addition
of ferrous chloride to the solvent mixture of ethanol/water. Crystals were obtained and
diffraction data were collected, but the intensities decreased rapidly, probably because of
desolvation of the crystals.

10.3 n-Octadecylammonium bromide

10.3.1 Thermal measurements

Thermal analysis was carried out by the technique of Differential Scanning Calorimetry
(DSC) using the Thermal Analysis 5000 instrument at the laboratory of Reckitt and
Coleman in Johannesburg.

DSC scans were measured for two samples of n-octadecylammonium bromide. The first
sample was obtained from crystallisation at room temperature, and the second from
crystallisation in a freezer. The heating and cooling rates used in the measurements were
5 °C per minute for both scans.

![DSC scan of room temperature sample of n-octadecylammonium bromide](image)

Fig 10.1: DSC scan of room temperature sample of n-octadecylammonium bromide
Fig 10.2: DSC scan of low temperature sample of \( n \)-octadecylammonium bromide

The first scan shows three transitions on heating but only one transition on cooling (Fig 10.1). If it is assumed that the sample was originally in the interdigitated phase as can be expected from the single crystal data, the first transition at 67.3 °C is the change to the \( \delta \) phase. The second transition occurs at approximately 75.0 °C, and is the transformation of the \( \delta \) phase to the \( \beta \) phase. (In DSC measurements of \( n \)-decylammonium chloride reported by Reynhardt et al [1992] the transition temperatures from the \( i \) to the \( \delta \), and the \( \delta \) to the \( \beta \) phases are also close, causing the exotherms to overlap. At 91° the \( \beta \) phase transforms to the \( \alpha \) phase, and the melting endotherm occurs at 107.3 °C.

On cooling only one exotherm is observed. The melted sample crystallises at 102.5°C. Reynhardt et al [1992] observed three transitions on cooling a sample of \( n \)-decylammonium chloride - first the transition from the \( \alpha \) to the \( \beta \), and then from the \( \beta \) to the \( \varepsilon \) phase. The rate at which our sample was cooled was the same as the rate reported by Reynhardt, so it is not clear why our sample showed only one crystallisation peak. It must be noted that the sample of \( n \)-decylammonium chloride was not melted, but only heated to the \( \alpha \) phase.
The presence of only one crystallisation peak in our DSC scan leads to the assumption that only one metastable phase is formed from the melt. This phase will probably transform to a more stable phase resembling the \( \varepsilon \) phase over a period of time.

The DSC scan of the sample of \( n \)-octadecylammonium bromide crystallised at a reduced temperature exhibits only two peaks on heating. The endotherms are broader, and the endotherms occurring in the range 60 to 78 °C in the room temperature scan may overlap in this scan to lead to only one broad endotherm. The endotherm at 107.3°C in the room temperature phase is virtually absent in the DSC measurement of the sample crystallised at a reduced temperature. Only a very small peak is visible. This must mean that this transition requires very little heat.

10.3.2 Single crystal structure determination:

The crystal structure of the interdigitated polymorph of this compound was determined from data collected from a single crystal obtained from \( n \)-hexane at room temperature. Systematic absences indicated spacegroups \( Cc \) or \( C2/c \). Volume calculations indicated that 4 molecules had to be placed in the unit cell, making \( Cc \) the most likely space group. The successful structure determination (using direct methods) substantiated this choice. The structure was refined using the computer program Shelx 97.

![Extended, all-trans chain in the interdigitated (i) phase of \( n \)-octadecylammonium bromide](image)
Fig 10.4: Unit cell contents projected to show interdigitation of chains

<table>
<thead>
<tr>
<th><strong>Single Crystal data</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical formula</strong></td>
<td>$\text{C}<em>{18}\text{H}</em>{27}\text{N}_3\text{Br}$</td>
</tr>
<tr>
<td><strong>Chemical formula weight</strong></td>
<td>$M_r = 343.35\text{g/mol}$</td>
</tr>
<tr>
<td><strong>Crystal class</strong></td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>$\text{C}1\text{c}1 \equiv \text{Cc}$</td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>4.804(6)</td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>58.21(6)</td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
<td>7.910(6)</td>
</tr>
<tr>
<td><strong>β (Å)</strong></td>
<td>105.84(8)</td>
</tr>
<tr>
<td><strong>V (Å$^3$)</strong></td>
<td>2212(3)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
</tr>
<tr>
<td><strong>$D_x (\text{Mg m}^3)$</strong></td>
<td>1.083</td>
</tr>
<tr>
<td><strong>Radiation type</strong></td>
<td>Mo Kα</td>
</tr>
<tr>
<td><strong>Wavelength (Å)</strong></td>
<td>0.7107</td>
</tr>
<tr>
<td><strong>θ range (°)</strong></td>
<td>3 to 26</td>
</tr>
<tr>
<td><strong>Temperature (K)</strong></td>
<td>293</td>
</tr>
<tr>
<td><strong>Crystal form</strong></td>
<td>Rectangular plate</td>
</tr>
<tr>
<td><strong>Crystal dimensions (mm)</strong></td>
<td>0.17 x 0.38 x 0.48</td>
</tr>
<tr>
<td><strong>Crystal colour</strong></td>
<td>Colourless</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Data collection</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diffractometer</strong></td>
<td>Philips PW1100 (4-circle)</td>
</tr>
<tr>
<td><strong>Detector</strong></td>
<td>Scintillation</td>
</tr>
<tr>
<td><strong>No. of measured reflections</strong></td>
<td>1009</td>
</tr>
<tr>
<td><strong>R_{int}</strong></td>
<td>0.890</td>
</tr>
<tr>
<td><strong>Range of h,k,l</strong></td>
<td>$-5 \leq h \leq 4; 0 \leq k \leq 60; -9 \leq l \leq 9$</td>
</tr>
</tbody>
</table>
Refinement

Refinement method  
Least squares on $F^2$

Goodness-of fit on $F^2$  
1.263

Final R indices  
0.089

R indices (all data)  
0.095

The molecular structure shows the carbon chain in an all-trans conformation (Fig 10.3 and Fig 10.4). Bond lengths and angles are listed in Table 10.1.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-C1</td>
<td>1.44(3)</td>
<td>N-C1-C2</td>
<td>92(2)</td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.61(4)</td>
<td>C1-C2-C3</td>
<td>115(2)</td>
</tr>
<tr>
<td>C2-C1</td>
<td>1.60(3)</td>
<td>C2-C3-C4</td>
<td>118(2)</td>
</tr>
<tr>
<td>C3-C4</td>
<td>1.47(3)</td>
<td>C3-C4-C5</td>
<td>114(2)</td>
</tr>
<tr>
<td>C4-C5</td>
<td>1.52(3)</td>
<td>C4-C5-C6</td>
<td>116(2)</td>
</tr>
<tr>
<td>C5-C6</td>
<td>1.46(3)</td>
<td>C5-C6-C7</td>
<td>120(2)</td>
</tr>
<tr>
<td>C6-C7</td>
<td>1.47(4)</td>
<td>C6-C7-C8</td>
<td>118(2)</td>
</tr>
<tr>
<td>C7-C8</td>
<td>1.52(3)</td>
<td>C7-C8-C9</td>
<td>115(2)</td>
</tr>
<tr>
<td>C8-C9</td>
<td>1.51(3)</td>
<td>C8-C9-C10</td>
<td>115(2)</td>
</tr>
<tr>
<td>C9-C10</td>
<td>1.44(3)</td>
<td>C9-C10-C11</td>
<td>117(2)</td>
</tr>
<tr>
<td>C10-C11</td>
<td>1.56(3)</td>
<td>C10-C11-C12</td>
<td>116(2)</td>
</tr>
<tr>
<td>C11-C12</td>
<td>1.48(3)</td>
<td>C11-C12-C13</td>
<td>117(2)</td>
</tr>
<tr>
<td>C12-C13</td>
<td>1.48(3)</td>
<td>C12-C13-C14</td>
<td>115(2)</td>
</tr>
<tr>
<td>C13-C14</td>
<td>1.56(3)</td>
<td>C13-C14-C15</td>
<td>112(2)</td>
</tr>
<tr>
<td>C14-C15</td>
<td>1.54(3)</td>
<td>C14-C15-C16</td>
<td>115(2)</td>
</tr>
<tr>
<td>C15-C16</td>
<td>1.48(3)</td>
<td>C15-C16-C17</td>
<td>115(2)</td>
</tr>
<tr>
<td>C16-C17</td>
<td>1.42(3)</td>
<td>C16-C17-C18</td>
<td>111(2)</td>
</tr>
<tr>
<td>C17-C18</td>
<td>1.61(4)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 10.1: Bond lengths and angles with e.s.d.'s

Refinement of the diffraction data yielded questionably long C-C bonds. The following bonds were longer than the 1.54 Å expected for a single carbon-carbon bond: C1-C2 →
1.61 Å; C2–C3 → 1.60 Å and C17–C18 → 1.61. However, as noted before, Nyburg also obtained C–C bond lengths of 1.59 Å and 1.66Å between the second and third, and third and fourth carbon atoms in the structure of di-n-octadecylammonium bromide [Nyburg, 1996]. Nyburg was not sure if this effect was real or if it was due to poor diffraction data.

The uncertainty in the bond lengths prompted us to recollect single crystal diffraction data from a different crystal of n-octadecylammonium bromide crystallized under similar conditions as the first. We also used a different diffractometer, namely the Siemens SMART system equipped with an area detector. Refinement of this second set of data resulted in similar bond lengths, with the same anomalous distances for the abovementioned three bonds. Therefore it seems that this effect is real. These long carbon-carbon bond lengths have only been observed for two n-octadecylammonium bromides and not for the -chlorides.

10.3.3 X-Ray Powder diffraction studies

Interdigitated polymorph

The presence of the long carbon-carbon bonds indicated by single crystal diffraction data prompted us to investigate the structural model further by other structural techniques, specifically fitting the powder pattern of the bulk sample by Rietveld refinement of the model obtained from the single crystal data. Two computer programs were employed, i.e. DBWS98 and WinMProf.

A powder diffraction pattern of a sample of n-octadecylammonium bromide crystallised under similar conditions as the single crystal was measured [Fig 10.5]. Data were recorded at room temperature on a Siemens D5000 X-ray powder diffractometer equipped with a scintillation detector. A glass capillary with an internal diameter of 1mm was used as a sample holder, and the sample irradiated with Cu Kα1 radiation. Data was collected for the 2θ range 2.2° to 60.0°. The measuring time was 60 seconds per step of 0.01°.
Fig. 10.5: Experimental powder diffraction pattern of interdigitated polymorph of $n$-octadecylammonium bromide.

Rietveld refinement by the program DBWS98 was employed to determine if the crystal structure obtained from the single crystal data solution was representative of the bulk sample. The experimental powder diffraction pattern and the pattern calculated from the single crystal structure, as well as a difference plot is shown in Fig 10.6. Observed and calculated peak positions are compared in Appendix 2.

Problems were experienced in the refinement of temperature factors (displacement factors) when using the program DBWS. It was observed that refinement of these temperature factors for individual atoms yielded negative values. The most probable cause is that the program assumes Bragg-Brentano geometry and flat plate samples. The geometry used in collecting experimental data, namely with a capillary sample increases the intensity at higher diffraction angles relative to that of a flat plate sample. DBWS corrects for this increase in high angle intensity resulting in a systematic error manifesting itself as a negative temperature factor.

The Rietveld Refinement of the model was, however, successful using the program DBWS98 if only a global thermal parameter was refined. The final R-values were:
\( R_p = 10.30 \)
\( R_{wp} = 14.34 \) and
\( S = 4.59 \)

The R-values are not as low as may be expected for normal Rietveld refinement, but considering the high R values obtained from the single crystal data, the refinement was deemed acceptable.

Considering the number of data points obtained from the powder diffraction pattern, the maximum number of parameters that could be refined yielding a ratio of 10 between parameters and observed data points, were 34. The background was described by a fifth order polynomial function and the peak shapes by a pseudo Voigt function.

The parameter turn on sequence was:

1. Scale factor
2. Background
3. Background
4. Zero displacement
5. \( W \)
6. \( N_A \)
7. Background
8. \( U \)
9. \( .a \)
10. \( .b \)
11. \( .c \)
12. \( .\beta \)
13. Background
14. \( N_B \)
15. \( V \)
Fig 10.6: Difference plot of Rietveld refinement of \( n \)-octadecylammonium bromide using the program DBWS (Plot by Dmplot)

Fig 10.7: Detailed difference plot of the complex region \( 15^\circ \) to \( 30^\circ \) \( 2\theta \) of calculated and experimental powder patterns after Rietveld refinement using the program DBWS.
High temperature phase:

To investigate the structure of the high temperature, non-interdigitated polymorph of \(n\)-octadecylammonium bromide, a sample was prepared by evaporating a solution of \(n\)-octadecylammonium bromide in hot methanol. The sample was heated on a hot plate until all the methanol was evaporated. Care was taken not to overheat after all the solvent has evaporated to prevent the decomposition of the compound. The powder diffraction pattern was measured under the same conditions as mentioned for the pattern of the interdigitated polymorph of \(n\)-octadecylammonium bromide (Fig 10.8). The pattern was recorded for the \(2\theta\) range 2.8\(^\circ\) to 68.3\(^\circ\).

![Fig 10.8: Powder diffraction pattern of sample crystallised from hot methanol](image)

By overlaying the powder diffractograms of the interdigitated phase with the pattern collected from the sample crystallised at high temperature (Fig 10.9), it is clear that some peaks appear in both patterns, indicating the presence of the interdigitated phase in the high-temperate sample. The additional peaks indicate one or more other phases, possibly the non-interdigitated \(\delta\) phase, and/or the \(\varepsilon\) phase.
Fig. 10.9: Powder diffraction patterns of interdigitated and high temperature samples of n-octadecylammonium bromide

Efforts to index the pattern using standard indexing procedures did not prove successful. The additional peaks in the low angular region indicate only one additional phase. These peaks could in fact be indexed manually as shown in Table 10.1.

<table>
<thead>
<tr>
<th>d</th>
<th>d/13.18495</th>
<th>p</th>
<th>1/p</th>
<th>x 6</th>
<th>index</th>
<th>d x index</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.37981</td>
<td>2.000751615</td>
<td>2</td>
<td>0.5</td>
<td>3</td>
<td>003</td>
<td>79.13943</td>
</tr>
<tr>
<td>19.93389</td>
<td>1.511866939</td>
<td>1.5</td>
<td>0.692984164</td>
<td>4</td>
<td>004</td>
<td>79.73556</td>
</tr>
<tr>
<td>15.60496</td>
<td>1.183543358</td>
<td>1.185</td>
<td>0.843881857</td>
<td>5</td>
<td>005</td>
<td>78.0248</td>
</tr>
<tr>
<td>13.18495</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>6</td>
<td>006</td>
<td>79.1097</td>
</tr>
</tbody>
</table>

Table 10.1: Indices of low angle reflections.

Eliminating the peaks resulting from the interdigitated phase, a list of the peaks corresponding to the other phase/ phases could be determined. Efforts to index this difference pattern using standard indexing programs did not prove to be successful. Despite the complexity of this pattern, the low angle reflections contribute information on the value of the $d(001)$ value of the major second polymorph. The average $d(001)$
value of the reflections listed in Table 10.1 is 79.0 Å. The $d(001)$ value for the interdigitated polymorph of $n$-octadecylammonium bromide is 58.33 Å. The fact that the $d(001)$ value for the high temperature form is larger than that of the interdigitated form most probably indicates a non-interdigitated packing for this high temperature form, resulting in thicker lamellas.

In order to solve the structure of this non-interdigitated polymorph by extracting structure factors, it will be necessary to measure the diffraction data of a sample containing only one polymorph. Further crystallisation experiments will have to be performed, and polymorphic characterisation techniques other than powder diffraction investigated.
10.4 n-Octadecylammonium chloride

10.4.1 Hot stage microscopy study

Hot stage microscopy studies were performed on an Olympus hot stage microscope. A crystal of \textit{n}-octadecylammonium chloride grown at room temperature from THF was heated from room temperature on the hot stage microscope. The pictures obtained when viewing images using polarised transmitted light at different temperatures are shown below.

1. Crystal initially at room temperature (4x)
2. Crystal initially at room temperature (10x)

2. Onset of solid state phase transition at 85.4°C
3. Progression of phase transition
3. Completion of phase transition at 87.2°C

4. Onset of second phase transition at 149°C

5. Melting at 159°C

6. Crystallisation after melting at 154°C

Even though the interdigitated (i) and non-interdigitated (δ) forms of n-octadecylammonium chloride are structurally different, the DSC measurements were the same for both forms [Scholtz, 1997]. Phase transitions were observed at 88°C and 116°C.

The room temperature polymorph for n-octadecylammonium chloride is the non-interdigitated δ phase. This phase transforms to the β phase on heating. The transition at approximately 85°C is most probably the transition of the δ to the β phase. The second phase transition is the transition of the β phase to the high temperature α phase. This transition occurs at 149°C. The α phase melts to a clear liquid at 159°C.
The phase transitions can be observed in great detail under the hot stage microscope. In both the observed transitions the morphology of the crystal changed considerably. In the first transition the smooth crystal surface became rough. After the second transition the crystal was waxy and soft due to the disorder present in the molecules.

Hot stage microscopy is a powerful technique to study solid state transformations in these type of long chain molecules. Due to the change in molecular orientation occurring during the phase transition, the morphology and appearance of the crystal change. This technique can be used to characterise a specific polymorph and is much quicker than powder diffraction. By noting the phase transitions occurring in a crystal at a specific temperature, the polymorphic form can be determined. This method will also indicate the presence of solvent molecules in the lattice if bubbles are observed on the surface of the crystal.

10.4.2 X-ray Powder diffraction

A powder sample of the interdigitated phase of \( n \)-octadecylammonium chloride could be obtained from crystallisation at reduced temperatures (\( T = 3^\circ C \)). Single crystals of good enough quality to determine the crystal structure could not be obtained. We have made an attempt to solve the crystal structure from powder diffraction patterns, so far without success.

Powder diffraction data was recorded for \( n \)-octadecylammonium chloride crystallised in a freezer (-3°C). Data were recorded on a Siemens D5500 diffractometer using a glass capillary as sample holder to minimise the effect of preferred orientation. The diffraction pattern is shown in Fig 10.10.
Fig 10.10: Powder diffraction pattern of the interdigitated, low temperature phase of n-octadecylammonium chloride

The experimental powder diffraction pattern of the low temperature polymorph of n-octadecylammonium chloride was indexed by the program TREOR90 (Werner et al.; 1985] in the indexing suite Crysfire. Only one solution with a high factor of merit of 21 was obtained. Calculated and observed reflections are compared in Table 10.2.
<table>
<thead>
<tr>
<th>H</th>
<th>K</th>
<th>L</th>
<th>2Theta (Exp.)</th>
<th>2Theta (Calc.)</th>
<th>2Theta (Diff.)</th>
<th>d (Exp.)</th>
<th>d (Calc.)</th>
<th>Intensity (Exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>3.551</td>
<td>3.593</td>
<td>-0.042</td>
<td>35.73702</td>
<td>24.57067</td>
<td>1022.03</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>2</td>
<td>7.133</td>
<td>7.19</td>
<td>-0.057</td>
<td>12.38365</td>
<td>12.28534</td>
<td>776.34</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>3</td>
<td>10.749</td>
<td>10.793</td>
<td>-0.044</td>
<td>8.22365</td>
<td>8.19022</td>
<td>821.09</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>4</td>
<td>14.4</td>
<td>14.408</td>
<td>-0.008</td>
<td>6.14588</td>
<td>6.14267</td>
<td>985.05</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>16.229</td>
<td>16.254</td>
<td>-0.024</td>
<td>5.45712</td>
<td>5.44898</td>
<td>944.19</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>2</td>
<td>17.601</td>
<td>17.596</td>
<td>0.005</td>
<td>5.0348</td>
<td>5.03618</td>
<td>1200.58</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>5</td>
<td>17.993</td>
<td>18.037</td>
<td>-0.043</td>
<td>4.92589</td>
<td>4.91413</td>
<td>1269.22</td>
</tr>
<tr>
<td>-1</td>
<td>0</td>
<td>3</td>
<td>18.524</td>
<td>18.558</td>
<td>-0.034</td>
<td>4.78585</td>
<td>4.77722</td>
<td>1414.61</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>3</td>
<td>19.499</td>
<td>19.531</td>
<td>-0.032</td>
<td>4.54873</td>
<td>4.54134</td>
<td>1409.2</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>3</td>
<td>19.561</td>
<td>19.531</td>
<td>0.03</td>
<td>4.53444</td>
<td>4.54134</td>
<td>1423</td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>19.831</td>
<td>19.867</td>
<td>-0.036</td>
<td>4.47344</td>
<td>4.46538</td>
<td>1652.01</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>20.349</td>
<td>20.349</td>
<td>0</td>
<td>4.36078</td>
<td>4.36078</td>
<td>1666.78</td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
<td>2</td>
<td>20.848</td>
<td>20.858</td>
<td>-0.009</td>
<td>4.25733</td>
<td>4.2555</td>
<td>14398.32</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>2</td>
<td>21.432</td>
<td>21.444</td>
<td>-0.012</td>
<td>4.14264</td>
<td>4.14038</td>
<td>1642.95</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>4</td>
<td>21.893</td>
<td>21.909</td>
<td>-0.016</td>
<td>4.05643</td>
<td>4.05351</td>
<td>1674</td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
<td>3</td>
<td>22.241</td>
<td>22.246</td>
<td>-0.005</td>
<td>3.99378</td>
<td>3.99285</td>
<td>9394.49</td>
</tr>
<tr>
<td>-1</td>
<td>0</td>
<td>5</td>
<td>23.339</td>
<td>23.307</td>
<td>0.032</td>
<td>3.80838</td>
<td>3.81348</td>
<td>1463.17</td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
<td>4</td>
<td>24.124</td>
<td>24.115</td>
<td>0.009</td>
<td>3.68622</td>
<td>3.68754</td>
<td>2195.52</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>0</td>
<td>24.458</td>
<td>24.46</td>
<td>-0.002</td>
<td>3.63657</td>
<td>3.63635</td>
<td>11341.37</td>
</tr>
<tr>
<td>-1</td>
<td>0</td>
<td>6</td>
<td>26.124</td>
<td>26.143</td>
<td>-0.019</td>
<td>3.40837</td>
<td>3.4059</td>
<td>901.45</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>5</td>
<td>27.54</td>
<td>27.536</td>
<td>0.005</td>
<td>3.23617</td>
<td>3.23672</td>
<td>834.09</td>
</tr>
<tr>
<td>-1</td>
<td>2</td>
<td>2</td>
<td>29.828</td>
<td>29.87</td>
<td>-0.042</td>
<td>2.99299</td>
<td>2.98888</td>
<td>821.58</td>
</tr>
<tr>
<td>-2</td>
<td>0</td>
<td>1</td>
<td>31.612</td>
<td>31.618</td>
<td>-0.006</td>
<td>2.82804</td>
<td>2.82752</td>
<td>1204.02</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>1</td>
<td>32.01</td>
<td>32.019</td>
<td>-0.009</td>
<td>2.79374</td>
<td>2.79298</td>
<td>950.02</td>
</tr>
<tr>
<td>-1</td>
<td>2</td>
<td>4</td>
<td>32.284</td>
<td>32.283</td>
<td>0.001</td>
<td>2.77066</td>
<td>2.77073</td>
<td>777.17</td>
</tr>
<tr>
<td>-2</td>
<td>0</td>
<td>3</td>
<td>32.902</td>
<td>32.909</td>
<td>-0.007</td>
<td>2.72002</td>
<td>2.71946</td>
<td>1055.29</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>3</td>
<td>34.091</td>
<td>34.06</td>
<td>0.031</td>
<td>2.62785</td>
<td>2.63014</td>
<td>1193.33</td>
</tr>
<tr>
<td>-2</td>
<td>0</td>
<td>4</td>
<td>34.145</td>
<td>34.145</td>
<td>0</td>
<td>2.62383</td>
<td>2.62381</td>
<td>1178.89</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>9</td>
<td>35.089</td>
<td>35.081</td>
<td>0.008</td>
<td>2.55335</td>
<td>2.55592</td>
<td>781.51</td>
</tr>
<tr>
<td>-1</td>
<td>0</td>
<td>9</td>
<td>35.7</td>
<td>35.707</td>
<td>-0.007</td>
<td>2.513</td>
<td>2.51253</td>
<td>701</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>8</td>
<td>36.181</td>
<td>36.168</td>
<td>0.013</td>
<td>2.48066</td>
<td>2.48155</td>
<td>742.87</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>10</td>
<td>38.64</td>
<td>38.648</td>
<td>-0.008</td>
<td>2.32827</td>
<td>2.32781</td>
<td>773.03</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>3</td>
<td>42.38</td>
<td>42.379</td>
<td>0.001</td>
<td>2.13109</td>
<td>2.13112</td>
<td>865.1</td>
</tr>
<tr>
<td>-3</td>
<td>1</td>
<td>2</td>
<td>50.071</td>
<td>50.094</td>
<td>-0.023</td>
<td>1.82027</td>
<td>1.81948</td>
<td>886.21</td>
</tr>
</tbody>
</table>

Table 10.2: Calculated and observed reflections

The unit cell dimensions obtained from indexing of the pattern agree very well with the dimensions reported for interdigitated structures in the literature (See Table 10.3). The \( c \) unit cell dimension increases linearly with the number of carbon atoms in the chain (see Fig. 10.11). The \( a \) and \( b \) unit cell dimensions stay almost constant with increasing \( n \).
Table 10.3: Cell parameters of interdigitated structures from the literature compared to the experimental cell parameters obtained for interdigitated \( n \)-octadecylammonium chloride.

<table>
<thead>
<tr>
<th>Structure</th>
<th>( a ) (Å)</th>
<th>( b ) (Å)</th>
<th>( c ) (Å)</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}<em>{10}\text{H}</em>{21}\text{NH}_3\text{Cl} )</td>
<td>5.6996</td>
<td>7.1638</td>
<td>15.4900</td>
<td>91.2970</td>
</tr>
<tr>
<td>( \text{C}<em>{12}\text{H}</em>{25}\text{NH}_3\text{Cl} )</td>
<td>5.6820</td>
<td>7.1860</td>
<td>17.7750</td>
<td>92.7500</td>
</tr>
<tr>
<td>( \text{C}<em>{18}\text{H}</em>{33}\text{NH}_3\text{Cl} )</td>
<td>5.6656</td>
<td>7.2727</td>
<td>24.6067</td>
<td>93.1010</td>
</tr>
</tbody>
</table>

Fig 10.11: Change in unit cell dimension \( c \) with number of carbon atoms for interdigitated \( n \)-alkylammonium chlorides

From Fig 10.10 it is clear that the unit cell dimensions for the isostructural \( n \)-alkylammonium chlorides can be predicted by a linear equation in the chain length range investigated. The following equations were derived to predict the unit cell dimensions of interdigitated \( n \)-alkylammonium chlorides:

\[
\begin{align*}
\text{b (Å)} &= 0.0138n + 7.0234 \\
\text{c (Å)} &= 1.1394n + 4.0991
\end{align*}
\]

The \( a \) unit cell dimension seem to be independent of the number of carbon atoms in the chain. The values predicted by these equations are compared to the experimental values in Table 10.4.
Table 10.4: Comparison between calculated and experimental unit cell dimensions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>b exp</th>
<th>b calc</th>
<th>c exp</th>
<th>c calc</th>
</tr>
</thead>
<tbody>
<tr>
<td>C10H21NH3Cl</td>
<td>7.1638</td>
<td>7.1615</td>
<td>15.49</td>
<td>15.4927</td>
</tr>
<tr>
<td>C12H25NH3Cl</td>
<td>7.186</td>
<td>7.1891</td>
<td>17.775</td>
<td>17.7714</td>
</tr>
<tr>
<td>C18H33NH3Cl</td>
<td>7.2727</td>
<td>7.2719</td>
<td>24.6067</td>
<td>24.6076</td>
</tr>
</tbody>
</table>

Despite the fact that only three data points were used to obtain the equations, resulting in a relatively high margin of error, there is a good agreement between the observed unit cell dimensions and the values calculated using the equations.

10.4.3 Rietveld Refinement

In order to determine a starting model for the Rietveld refinement of n-octadecylammonium chloride, the two interdigitated structures reported in the literature were compared namely that of n-decylammonium chloride and n-dodecylammonium chloride.

The powder diffraction patterns of n-decylammonium chloride and n-dodecylammonium chloride were calculated using the fractional co-ordinates reported in the literature. The Rietveld refinement program DBWS97 was employed. The calculated patterns are illustrated in Fig. 10.12 and Fig 10.13.
Fig 10.12: Calculated powder diffraction pattern of interdigitated polymorph of \( n \)-decylammonium chloride (Program DBWS)

Fig 10.13: Calculated powder diffraction pattern of interdigitated polymorph of \( n \)-dodecylammonium chloride (Program DBWS)
The iso-structurality of the three low temperature interdigitated polymorphs of \( n \)-decylammonium chloride, \( n \)-dodecylammonium chloride and \( n \)-octadecylammonium chloride is clear from the similarity in powder diffraction patterns (See Fig 10.9, 10.11 and 10.12). All three diffraction patterns contain three strong peaks representing planes containing high electron density. This means that the packing of \( n \)-octadecylammonium chloride in the unit cell must be similar to that found for \( n \)-decylammonium chloride and \( n \)-dodecylammonium chloride. The projected packings of \( n \)-dodecylammonium chloride are shown in the Fig 10.14.

Fig 10.14: Packing of \( n \)-dodecylammonium chloride in the unit cell.

It must be noted, however, that the three strong peaks in the range \( 20^\circ \text{<} 2\theta < 26^\circ \) have different indices in the three patterns. This is probably due to a different tilt angle of the chain molecule relative to the unit cell, leading to different planes containing high electron density.

In the interdigitated phase of the structures reported in the literature, the carbon atoms are in a \textit{trans} configuration, with space group \( P2_1 \).
After various efforts to extrapolate the structure of \( n \)-octadecylammonium chloride geometrically form the structures of \( n \)-decylammonium chloride and \( n \)-dodecylammonium chloride, no satisfactory model for Rietveld refinement could be obtained.

In a different approach the Le Bail method was used to extract the structure factors from powder data, from which single crystal methods for structure determination could be employed. No structure could so far be solved, but further work is in progress.
10.5 \( n \)-Octadecylammonium iodide

10.5.1 Cell dimensions of \( C_{18}H_{37}NI \) crystallised in the presence of ferrous chloride

Cell dimensions and space group were determined for a crystal of \( n \)-octadecylammonium iodide crystallised form a mixture of ethanol and aqueous ferrous chloride. The structure of \( n \)-undecylammonium chloride monohydrate [Silver et al, 1996] was determined from a crystal grown under similar conditions. The diffraction data used to solve the structure were, however, collected at reduced temperature (no indication was given of the specific temperature).

Our data were collected at room temperature, but it was soon clear from the fall-off of intensities that the crystal was undergoing some sort of decomposition. The most probable process is the loss of water from the crystal lattice. A solution to this problem would be the use of a cryostat to collect data at lower temperatures, and thereby reducing crystal decomposition.

Even though the crystal decomposition prevented the collection of diffraction data suitable for structure determination, it gave an indication that solvent was present in the crystal structure, and that it is possible to obtain hydrated \( n \)-alkylammonium halides. The apparent effect of addition of ferrous chloride was the incorporation of water molecules in the crystal lattice. No other reports were found in the literature on the effect of metal ions on the crystallisation of \( n \)-alkylammonium halides, and this is definitely a field of research worth investigating.

Even though the structure could not be solved, information on cell dimensions and symmetry could be obtained from the data.

\( n \)-Octadecylammonium iodide monohydrate

**Monoclinic**

<table>
<thead>
<tr>
<th>Space group</th>
<th>( Clc1 ) (Probably)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a ) (Å)</td>
<td>11.841(4)</td>
</tr>
<tr>
<td>( b ) (Å)</td>
<td>10.20(4)</td>
</tr>
<tr>
<td>( c ) (Å)</td>
<td>22.236(4)</td>
</tr>
</tbody>
</table>
No structure determination of an \( n \)-alkylammonium iodide could be located in the literature, let alone the structure of a hydrate of these compounds. The cell dimensions as determined could not be compared to any known values, indicating the necessity to investigate both the structure of \( n \)-alkylammonium iodides, and the effect of incorporation of a water molecule on the packing.

10.5.2 Thermal investigations

![DSC scan of \( n \)-octadecylammonium iodide](image)

**Fig 10.15: DSC scan of \( n \)-octadecylammonium iodide**

A DSC scan of a sample of \( n \)-octadecylammonium iodide crystallised from methanol at room temperature is shown in Fig 10.15. Even though no reports on the structures or thermal behaviour of \( n \)-alkylammonium iodides are available in the literature, the obtained DSC scan is similar to what is observed for other \( n \)-alkylammonium halides. It can thus be assumed that the thermal behavior of \( n \)-octadecylammonium iodide is similar
to that of other \( n \)-alkylammonium halides. If this assumption is valid, the observed transformations may be explained as follows:

The scan exhibits four endotherms. The sample is initially in the low temperature, interdigitated phase. On heating a transition occurs to the non-interdigitated \( \delta \) phase at 69.38 °C. This phase transforms to the \( \beta \) phase at 73.34°C, which, in turn, transforms to the \( \alpha \) phase at 82.87 °C. The sample melts at 92.18 °C.

The scan resembles the scan of the room temperature sample (interdigitated polymorph) of \( n \)-octadecylammonium bromide (Fig 10.1).
Section C

Discussion and Conclusions
Chapter 11

Discussion and Conclusions

11.1 n-Octadecylammonium halides

Various experimental techniques were employed to investigate the structural characteristics and thermal behavior of n-octadecylammonium halides.

11.1.1 Structural investigations

Single crystal structure: n-Octadecylammonium bromide (C\textsubscript{18}Br)

The single crystal structure of the interdigitated, stable polymorph of this compound was determined from a crystal grown at room temperature.

The molecule is virtually in the all-trans conformation. Distortions are present in the hydrocarbon subcell however, and the molecule is slightly bent perpendicular to the zig-zag plane of carbon atoms. This distortion is indicated by the deviation of the C-C bond lengths and C-C-C angles from the expected values of 1.54 Å and 112°. The C1-N bond is out of the plane of the rest of the molecules as can be seen in Fig. 11.1.

Fig 11.1: Projections of molecule to indicate bent molecule.
The hydrocarbon subcell is monoclinic with the zig-zag planes parallel (M//).

Fig. 11.2: Hydrocarbon subcell (a) Projection to show subcell (b) schematic representation of M// subcell

Fig 11.3: Arrangement of atoms in the polar region
The arrangement of atoms in the polar region is indicated in Fig 11.3. Four NH$_3^+$ groups and two methyl groups surround the bromine atom forming an approximately octahedral cavity. One nitrogen atom is above and one below the bromine atom. Hydrogen bonds are formed between the NH$_3^+$-group and the bromine atom [See Fig 13.4].

![Diagram of hydrogen bonds](image)

**Fig 11.4:** Hydrogen bonds formed between bromine and NH$_3^+$-groups

**Comparison with similar structures**

The only other structure of a long chain interdigitated $n$-octadecylammonium bromide reported in the literature is that of $n$-dodecylammonium bromide (C$_{12}$Br) [Lunden, 1974]. The powder pattern of this compound was calculated from the reported fractional coordinates using the computer program DBWS98. The input file is given in Appendix 1.
Fig 11.5: Calculated powder diffraction pattern of \( n \)-dodecylammonium bromide

[Plot by DMPlot].

It is clear by comparison of the calculated powder diffraction pattern of \( n \)-dodecylammonium bromide and that of the experimental pattern of the interdigitated polymorph of \( n \)-octadecylammonium bromide (Fig 10.6) that the interdigitated structures are not isostructural. It is still helpful to compare some of the structural characteristics of the two interdigitated polymorphs.
Another structure that is related to that of \( n \)-octadecylammonium bromide is that of \( \text{di-n-octadecylammonium bromide} \ (\text{C}_{18})_2\text{Br} \) reported by Nyburg [1996]. As mentioned previously, this structure also shows long C-C bonds.

\[
\begin{array}{ccc}
\text{C}_{18}\text{Br} & \text{C}_{12}\text{Br} & (\text{C}_{18})_2\text{Br} \\
\text{N-Cl (Å)} & 1.4431 & 1.482 & 1.50 \\
\text{N-Br (Å)} & 3.39^* & 3.34^* & - \\
\end{array}
\]

* Average of bonds

Table 11.1: Comparison of selected bond lengths

Fig 11.6: Distribution of C-C bond lengths

The average value of all the C-C bond lengths is 1.51 Å. This value compares well to the value of 1.54 Å. The average of the bonds without the three long C-C bonds is 1.49 Å. The bonds do not show a Gaussian distribution.

A possible explanation of the long C1-C2, C2-C3 and C17-C18 bonds is the formation of hydrogen bonds between C1 and the bromide ion. In Fig 11.4 the conformation of the atoms near the ends of the molecules are shown. It seems that C1 is displaced towards the bromide ion. This may indicate interaction between C1 and
Br⁻ via hydrogen bonds. The long C17-C18 bond may also indicate a displacement of C18 towards the bromide ion, and interaction via hydrogen bonds.

Weak hydrogen bonds have been reported in the literature [Braga et al, 1998, Braga and Grepioni, 1998]. The existence of a proper hydrogen bond involving a carbon atom has been debated for a long time. In recent years more and more evidence suggesting the existence of these hydrogen bonds has been found. Hydrogen bonds of the type C-H---O are observed in organometallic compounds. Hydrogen bonds of carbon atoms are generally much weaker than other hydrogen interactions such as O-H—H or N-H—N.

Another possibility of the existence of hydrogen bonds between carbon atoms of long chain molecules is the crystallization of methyl octadecanoate in dimers. This behavior is similar to what is found for fatty acids where hydrogen bonds are formed between the carboxyl groups. Ethyl heptadecanoate does not crystallise in dimers. It may be that in methyl octadecanoate, the methyl groups of the ester groups interact via hydrogen bonds.

At this stage it is too early to definitely say if the long bonds are due to the formation of hydrogen bonds involving the carbon atoms. Similar compounds should be investigated, and if these effects are also present, a model of the hydrogen bonding network may be developed.

The long carbon-carbon bond lengths may also point to the presence of a defect in the chain. If the temperature of crystallization is below, but close to the temperature above which the most stable polymorph of n-octadecylammonium bromide is the non-interdigitated δ phase, the long bonds may be the onset of a kink in the molecule. At the specific temperature the molecule does not have a sufficiently large diameter to crystallize in the non-interdigitated state, and the most stable polymorph is still interdigitated. The molecule may, however, still posses some disorder and conformational flexibility, resulting in a defect in the chain, indicated by the long carbon-carbon bond lengths.
Thermal investigations

The thermal measurements made on n-octadecylammonium bromide and iodide have been reported in Chapter 10. The samples investigated were initially in the low temperature, stable, interdigitated polymorph. On heating transitions were observed to the non-interdigitated δ phase. This phase, in turn, transforms to the β phase. The β phase transforms to the α phase before the sample melts. This behavior is what is expected for n-octadecylammonium halides. The hot stage microscopy study of the room temperature polymorph of n-octadecylammonium chloride shows only two solid state transformations before melting of the crystal. From single crystal data [Scholtz, 1997] it is known that this sample is initially in the non-interdigitated δ phase, and transforms firstly to the β and then to the α form before melting.

The phase transitions of n-decylammonium chlorides have been investigated extensively [Kind et al, 1982; Seliger, 1983; Schenk et al, 1989; Reynhardt, 1992], and may be seen as a model for the thermal behavior of other n-alkylammonium halides. From the above measurements it can be deduced that the thermal behavior of n-octadecylammonium halides is similar to that of n-decylammonium chloride, and thus similar to what is expected for n-alkylammonium halides.

Powder diffraction investigations

The powder diffraction patterns of the interdigitated polymorphs of n-octadecylammonium chloride and -bromide were measured.

The structure of interdigitated n-octadecylammonium bromide was known from a crystal determination, and was employed to investigate the applicability of Rietveld refinement to these types of compounds. The calculated and experimental patterns were similar, indicating the applicability of the structural model to the bulk of the sample obtained from crystallization at room temperature. This refinement also yielded instrumental parameters, peak shapes and peak widths characteristic of n-octadecylammonium halides. These parameters will be used in future structure determinations of novel structures from powder diffraction data.
11.2 Fatty esters

11.2.1 Methyl-, ethyl and propyl esters

Our group investigated the thermal behavior of methyl heptadecanoate. Because only esters of even fatty acids are frequently encountered in nature, thermal investigations of esters of odd fatty acids have not been reported in literature. The general trend seen in the behavior of esters of even numbered fatty acids may not be applicable to the esters of odd fatty acids.

The methyl, ethyl and propyl esters of even numbered fatty acids (n = 16, 18) crystallize in layers with the molecule in an extended conformation. The C-O-C group is basically an extension of the carbon chain, with the replacement of a carbon with O having little effect on the chain conformation. The C-O-C angle is in the range of 108 – 115° [Mathieson and Welsh, 1965], similar to the C-C-C angle of approximately 112°. The C=O group and the C atom attached to the ester O, is in a \textit{cis} configuration. Methyl esters crystallize in dimers, probably due to the possibility of interaction between the terminal methyl groups. Ethyl esters crystallize in layers of single molecules.

By comparing the unit cell dimensions of the monoclinic form of methyl octadecanoate, ethyl octadecanoate and propyl octadecanoate, it can be seen that the \(a\) and \(b\) axes have similar dimensions. The \(c\) axis differs with the length of the alkyl chain next to the carboxyl group, and whether the molecules pack as dimers or as single molecules in a layer.
From crystallization at reduced temperatures two crystalline forms can be obtained for the methyl esters: a monoclinic form where the axes of the molecules are parallel, and an orthorhombic form where the axis of molecules forming a dimer are parallel, but consecutive dimers are related by a twofold rotation axis in the ac plane. This may possibly be a case of polytypism. For ethyl esters only a monoclinic form has been reported. Because dimers are not formed, it would not be possible to form a modification resembling the polytypic modification of methyl esters.

When methyl and ethyl esters are heated, a solid state phase transition to another modification occurs just below the melting point. The structure of this modification has not been reported yet. For methyl esters the long spacing of this high temperature modification corresponds to a tilted, single molecular layer. From the melt another monoclinic form is obtained. The structure of this form has not been reported. This monoclinic form slowly transforms to the more stable monoclinic form obtained from solution crystallization with time. It is clear that with crystallization from the melt the kinetically favored polymorph is formed, and with crystallization from solution under equilibrium conditions, the more stable polymorph is obtained.

We investigated the thermal behavior of methyl heptadecanoate by DSC measurements (See Fig’s 9.1 to 9.4). The thermal behavior reported above of methyl...
octadecanoate was also observed for the methyl ester of \( n \)-heptadecanoic acid. In the first DSC scan only one melting endotherm is observed. The second DSC scan, and consecutive scans, exhibit two melting endotherms. The sample used for the first scan was crystallized from solution. The sample is melted in the first heating run and then crystallizes from the melt. The second heating run is thus from a sample obtained from melt crystallization. The crystallization from the melt result in a different polymorphic form than the one obtained from solvent crystallization. This behavior is also exhibited by other long chain systems, for example \( n \)-alkylammonium halides.

Two explanations may be given for the lack of a solid state transformation endotherm exhibited by the solution-crystallized sample. Firstly it is possible that this form does not undergo a solid state transformation before melting. Secondly, this form may exhibit a solid state transformation before melting, requiring much less energy than the solid state transformation of the melt-crystallized sample, with the instrument unable to resolve this peak.

The melt-crystallized sample shows two endotherms with increased temperature. The high temperature endotherm is the melting endotherm.

There are two possible interpretations of the low temperature endotherm:

i) that the first (smaller) endotherm indicates the transformation to a metastable structure, and the second (large) melting endotherm corresponds to the actual melting of the sample.

ii) that there are two different structures with different melting points present in the sample and that these two structures are unable to form a solid solution.

The first explanation is most likely, because it corresponds to the thermal behavior expected for methyl esters of acids with an odd number of carbon atoms, namely the transformation to a high temperature modification just below melting point.
11.2.2 Symmetrical esters: Hexadecyl hexadecanoate

Very little data are available in the literature on the structures of di-esters of fatty acids. The data available is not very recent, or from symmetrical esters of an even fatty acid. It has been reported in the literature [Dorset, 1976], that hexadecyl hexadecanoate crystallizes in both a monoclinic and an orthorhombic modification, depending on crystallization conditions. The $a$ and $b$ unit cell dimensions of the monoclinic modification agree well with the $a$ and $b$ dimensions of the monoclinic modification of methyl, ethyl and propyl octadecanoate, as well as the values obtained for octadecyl octadecanoate and hexadecyl octadecanoate by Sutula and Bartell [1962].

<table>
<thead>
<tr>
<th>Esters</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>beta</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octadecyl octadecanoate</td>
<td>5.56</td>
<td>7.53</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hexadecyl octadecanoate</td>
<td>5.65</td>
<td>7.40</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dodecyl dodecanoate</td>
<td>5.68</td>
<td>7.50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hexadecyl hexadecanoate</td>
<td>5.59</td>
<td>7.46</td>
<td>79.40</td>
<td>91.56</td>
</tr>
<tr>
<td>Methyl octadecanoate</td>
<td>5.61</td>
<td>7.33</td>
<td>106.60</td>
<td>116.60</td>
</tr>
<tr>
<td>Ethyl octadecanoate</td>
<td>5.59</td>
<td>7.40</td>
<td>57.10</td>
<td>118.50</td>
</tr>
<tr>
<td>Propyl octadecanoate</td>
<td>5.59</td>
<td>7.39</td>
<td>30.00</td>
<td>119.20</td>
</tr>
</tbody>
</table>

Table 11.2: Comparison of unit cell dimensions of certain fatty esters

These similar $a$ and $b$ dimensions possibly indicate a similar packing of the chains in the unit cell in one projection. The difference in chain length, and formation of dimers influence the $c$ cell dimension.

From indexing a powder diffraction pattern, we could obtain the unit cell dimensions of an orthorhombic modification of heptadecyl heptadecanoate. The unit cell dimensions are:

Orthorhombic

\[a = 4.5717 \text{ Å}\]
\[b = 4.4810 \text{ Å}\]
\[c = 41.2513 \text{ Å}\]

The $a$ and $b$ unit cell parameters of an orthorhombic modification of hexadecyl hexadecanoate were reported by Dorset [1976] as $a = 7.45$ Å and $b = 4.97$ Å.
It can be expected that the packing of molecules in the two crystal lattices of hexadecyl hexadecanoate and heptadecyl heptadecanoate would be similar because both compounds are symmetrical fatty esters containing an even number of carbon atoms in the molecule. But the odd-even effect may still influence the packing. The additional two carbon atoms at the end of each alkyl chain in heptadecyl heptadecanoate may result in a different packing of terminal methyl groups at the lamellar interface than what is found for hexadecyl hexadecanoate.

The \( b \) unit cell dimension of hexadecyl hexadecanoate is similar to our value of 4.57 Å for heptadecyl heptadecanoate, but the \( a \) dimension differs considerably. This probably indicates similar packing of the two compounds in one projection, but different packing in the other projection due to the odd-even effect.

The \( c \) unit cell dimension of 41.25 Å compares well with the \( c \) dimension predicted for the corresponding \( n \)-alkane. If the O atom is assumed to have the same conformation as a C atom, it can be approximated as part of the carbon chain. The length of the molecule would then be similar to that of a normal alkane with 35 carbon atoms in the molecule.

The \( d(001) \) value (and \( c \) unit cell dimension) for the orthorhombic modification of \( n-C_{35}H_{72} \) was predicted by Nyburg and Potworowski [1973] as 46.43 Å. The calculated \( c \) unit cell dimension of of \( n-C_{35}H_{72} \) using the equation of Chevallier et al [1999] is 46.41 Å. If it is assumed that the presence of the ester group in the chain results in a shorter molecule than the corresponding \( n \)-alkane, our \( c \) unit cell dimension value of 41.25 Å compares well with that of the corresponding \( n \)-alkane.

The effect of the ester group in the long chain can be investigated by comparing the \( c \)-unit cell dimension of the orthorhombic modification of methyl octadecanoate [MacGillavry and Wolthuis-Spuy, 1970] with that of the orthorhombic modification of the \( n \)-alkane \( C_{20}H_{42} \). The \( c \) unit cell dimension of methyl octadecanoate was reported as 95.14 Å. The \( c \) unit cell dimension of orthorhombic \( n-C_{20}H_{42} \) was reported by Nyburg and Potworowski [1973] as 54.49 Å. However, the unit cell of methyl octadecanoate contains two molecules in the \( c \)-axis direction, thus corresponding to twice the unit cell dimension of \( n-C_{20}H_{42} \) - 108.99 Å. The effect of the ester group in
the molecule is to shorten the molecule and consequently the \( c \) unit cell dimension of
the ester relative to that of the \( n \)-alkane if both compounds are in the orthorhombic
modification.

The need to investigate the structural and thermal behavior of esters of fatty acids is
clear from the small amount of data available from the literature. The fact that these
compounds are frequently encountered in natural waxes shows their importance in
influencing the properties of natural waxes, and the derived products.

Most of the available articles on the structures and packing of these esters are quite
old. Since these investigations were done, instruments have improved considerably.

This indicates the need to investigate these compounds using single crystal diffraction
techniques in order to determine the three dimensional molecular packing, and not
only projections on planes.

At this stage it would be very optimistic to predict structures of novel esters based on
extrapolation of the old literature. There are too many unknown parameters.

Many questions are still left unanswered, and can only be speculated on:

i ) Why do methyl esters form dimers, but not ethyl esters?

iii) What is the structure of the phase formed just below the melting point of these
esters? Is it hexagonal similar to the structure found for the \( n \)-alkanes?

iv) What is the effect of the thermal history of the sample on the thermal
behavior, and how reliable is the thermal investigations of early researchers.

Many authors claimed that certain expected peaks on DSC scans were absent,
but could this be a result of insensitive instruments not detecting these
transitions? Many of the early structure determinations were only projections
determined from photographs. How will these structures compare with three-
dimensional single crystal structures? Many early researches extrapolated one
structure to determine another. What if the initial structure was not reliable
and contained errors? How much weight can be attributed to these structures?

In order to be able to answer these questions, structures of esters must be determined
and a general trend identified. Future work of our group includes the low temperature
structure determination of methyl heptadecanoate and ethyl heptadecanoate. This will
shed light on the role of the odd-even effect in the structures of esters. Three-
dimensional structures of the two-dimensional projections reported in the literature
have to be determined. Investigation of other di-esters (for example octadecyl
octadecanoate) must be conducted. This will lead to a better understanding of the
molecular forces directing the packing, as well as the effect of the number of carbons
in the alkyl groups, and the parity of the carbons.
Chapter 12
Future Work

Various interesting possibilities for future work have been identified. These are briefly discussed below.

12.1 n-Alkylammonium halides

- Because no report of the structure of an n-alkylammonium iodide could be found in the literature, it will prove interesting to solve the structure of n-octadecylammonium iodide form single crystal data. Much effort will be put into the crystallization of this compound at various environmental conditions to obtain different polymorphs. If no good quality single crystals can be obtained, the compound can be investigated by powder diffraction and computational techniques. If the structure is solved, the role of the halide anion on the packing of the long chain molecules will be better understood. The series of n-octadecylammonium chloride, -bromide and -iodide will highlight the effect of increase in anion size.

- The crystal structure of the δ phase of n-octadecylammonium chloride has been determined [Scholtz, 1997]. We succeeded in indexing a powder pattern of the interdigitated polymorph of this compound. Attempts to solve the structure of the interdigitated phase by geometrical extrapolation and extraction of structure factors have proved unsuccessful up to this day. More effort will, however, still be put into solving the structure. If the structure can be refined, a better understanding of the mechanism of the phase transition of the interdigitated i-phase to the non-interdigitated δ phase will be obtained.

- The effect of incorporation of water molecules into the n-alkylammonium halide lattice by hydrogen bond will be investigated further. The effect of the presence of FeCl₂ in the solution will also be investigated. Hot stage microscopy studies of the crystals obtained will indicate the presence of water in the lattice. If a single
crystal of good quality grown under these conditions is obtained, data will be collected at a lower temperature to inhibit the loss of water from the lattice.

- Molecular modeling to determine the relative energies of different molecular conformations in the lattice, and relative energies of the different lattices of polymorphic forms of \( n \)-octadecylammonium halides will aid in the understanding of the factors influencing the packing of molecules in the crystal.

- The effect of the number of carbon atoms in the alkyl chain will become clear if the structures of \( n \)-heptadecylammonium halides are compared to those of \( n \)-octadecylammonium halides. The synthesis of \( n \)-heptadecylamine using heptadecanoic acid as starting material will be investigated. The structure and thermal behavior of these \( n \)-heptadecylammonium halides can be investigated by various instrumental techniques.

### 12.2 Fatty esters

- Because of the problems experience with working with the methyl- and ethyl esters of \( n \)-heptadecanoic acid due to their low melting point, it has been decided to focus our future investigations on determining the structures of symmetrical esters including hexadecyl hexadecanoate, heptadecyl heptadecanoate and octadecyl odtadecanoate. If good quality single crystals of these compounds can be obtained, the structure can by solved by single crystal X-ray diffraction. If single crystals cannot be obtained, it will be attempted to extrapolate the structure of these symmetrical esters from the powder diffraction data using the structures of \( n \)-alkanes with one more carbon atom in the molecules than the symmetrical esters as starting model.
References


Bernal, J.D. (1932). *Z. Kristall.* 83, 153-155


Appendix 1

Input files for computer programs
Program: DBWS98

1. Input file for Rietveld refinement of interdigitated polymorph of n-octadecylammonium bromide using fractional coordinates from single crystal refinement

C18NBr Heksaan Opgeneem by Unisa - eerste patroon

0 5 1 0 0 0 1 0 1 0
00111 10010 10000 000
1.54050 1.54050 .00000 10.0000 8.0000 .9764 .0000 15.0000 .0000
5 .10 .90 .90 .90 .90

RELAX P_CALC
21

-1.0607 .0000 .0000 .0000 .0000 1.0000 .0000 ZER DISP TRANS

pq rt
41.0000 .0000 .0000 .0000 .0000 .0000 .0000

388.52 -32.42 242.42 -106.36 12.14 .00 BACKGROUND

21.0000 31.0000 71.0000 131.0000 211.0000 .0000 CODEWORDS

C18NBr
1

20 4 1.0000 .001.00 .00

AFQPA PREFDIR
C1C1

SPACE GROUP

Br 4 BR .20960 .01816 .09770 4.00000 1.00000 LBL M NTYP x

y z B So

.00 .00 .00 .00 .00 .00 CODEWORDS

.00 .00 .00 .00 .00 .00 CODEWORDS

.00 .00 .00 .00 .00 .00 CODEWORDS

.00 .00 .00 .00 .00 .00 CODEWORDS

C1 4 C -14634 -.04237 -.0930 4.00000 1.00000 LBL M NTYP x

y z B So

161.00 171.00 181.00 .00 .00 .00 CODEWORDS

.00 .00 .00 .00 .00 .00 CODEWORDS

.00 .00 .00 .00 .00 .00 CODEWORDS

.00 .00 .00 .00 .00 .00 CODEWORDS

C2 4 C -.26506 -.06288 .01029 4.00000 1.00000 LBL M NTYP x

y z B So

191.00 .00 201.00 .00 .00 .00 CODEWORDS

.00 .00 .00 .00 .00 .00 CODEWORDS

.00 .00 .00 .00 .00 .00 CODEWORDS

.00 .00 .00 .00 .00 .00 CODEWORDS

C3 4 C -.18879 -.08652 -.07864 4.00000 1.00000 LBL M NTYP x

y z B So

0.00 .00 .00 .00 .00 .00 CODEWORDS

.00 .00 .00 .00 .00 .00 CODEWORDS

.00 .00 .00 .00 .00 .00 CODEWORDS

.00 .00 .00 .00 .00 .00 CODEWORDS

C4 4 C -.32362 .10800 -.05444 4.00000 1.00000 LBL M NTYP x

y z B So

0.00 .00 .00 .00 .00 .00 CODEWORDS

.00 .00 .00 .00 .00 .00 CODEWORDS

.00 .00 .00 .00 .00 .00 CODEWORDS

.00 .00 .00 .00 .00 .00 CODEWORDS

C5 4 C -.18652 -.12958 -.09869 4.00000 1.00000 LBL M NTYP x

y z B So

0.00 .00 .00 .00 .00 .00 CODEWORDS

.00 .00 .00 .00 .00 .00 CODEWORDS

.00 .00 .00 .00 .00 .00 CODEWORDS

.00 .00 .00 .00 .00 .00 CODEWORDS
<table>
<thead>
<tr>
<th>C6</th>
<th>4 C</th>
<th>y z B So</th>
<th>-.33350</th>
<th>-.15147</th>
<th>-.08486</th>
<th>4.00000</th>
<th>1.00000</th>
<th>LBL M NTYP x</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CODEWORDS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BETAS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td>C7</td>
<td>4 C</td>
<td>y z B So</td>
<td>-.18891</td>
<td>-.17335</td>
<td>-.10106</td>
<td>4.00000</td>
<td>1.00000</td>
<td>LBL M NTYP x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CODEWORDS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BETAS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td>C8</td>
<td>4 C</td>
<td>y z B So</td>
<td>-.33929</td>
<td>-.19542</td>
<td>-.07400</td>
<td>4.00000</td>
<td>1.00000</td>
<td>LBL M NTYP x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CODEWORDS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BETAS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td>C9</td>
<td>4 C</td>
<td>y z B So</td>
<td>-.19469</td>
<td>-.21707</td>
<td>-.11283</td>
<td>4.00000</td>
<td>1.00000</td>
<td>LBL M NTYP x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CODEWORDS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BETAS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td>C10</td>
<td>4 C</td>
<td>y z B So</td>
<td>-.33394</td>
<td>-.23802</td>
<td>-.08535</td>
<td>4.00000</td>
<td>1.00000</td>
<td>LBL M NTYP x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CODEWORDS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BETAS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td>C11</td>
<td>4 C</td>
<td>y z B So</td>
<td>-.18430</td>
<td>-.26101</td>
<td>-.11179</td>
<td>4.00000</td>
<td>1.00000</td>
<td>LBL M NTYP x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CODEWORDS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BETAS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td>C12</td>
<td>4 C</td>
<td>y z B So</td>
<td>-.33499</td>
<td>-.28240</td>
<td>-.08738</td>
<td>4.00000</td>
<td>1.00000</td>
<td>LBL M NTYP x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CODEWORDS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BETAS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td>C13</td>
<td>4 C</td>
<td>y z B So</td>
<td>-.18982</td>
<td>-.30432</td>
<td>-.10630</td>
<td>4.00000</td>
<td>1.00000</td>
<td>LBL M NTYP x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CODEWORDS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BETAS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td>C14</td>
<td>4 C</td>
<td>y z B So</td>
<td>-.35370</td>
<td>-.32625</td>
<td>-.07379</td>
<td>4.00000</td>
<td>1.00000</td>
<td>LBL M NTYP x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CODEWORDS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BETAS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td>C15</td>
<td>4 C</td>
<td>y z B So</td>
<td>-.19635</td>
<td>-.34842</td>
<td>-.10068</td>
<td>4.00000</td>
<td>1.00000</td>
<td>LBL M NTYP x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CODEWORDS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BETAS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td>C16</td>
<td>4 C</td>
<td>y z B So</td>
<td>-.33661</td>
<td>-.37008</td>
<td>-.06960</td>
<td>4.00000</td>
<td>1.00000</td>
<td>LBL M NTYP x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CODEWORDS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BETAS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td>C17</td>
<td>4 C</td>
<td>y z B So</td>
<td>-.17983</td>
<td>-.39040</td>
<td>-.08130</td>
<td>4.00000</td>
<td>1.00000</td>
<td>LBL M NTYP x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CODEWORDS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BETAS</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td>Codewords</td>
<td>Betas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>-------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.00 .00 .00 .00 .00</td>
<td>.00 .00 .00 .00 .00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C18 4 C</td>
<td>-.35925 -.41298 -.05984 4.00000 1.00000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>y z B So</td>
<td>.00 .00 .00 .00 .00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.00 .00 .00 .00 .00</td>
<td>.00 .00 .00 .00 .00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N 4 N</td>
<td>-.30405 -.02361 .01302 4.00000 1.00000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>y z B So</td>
<td>.00 .00 .00 .00 .00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.00 .00 .00 .00 .00</td>
<td>.00 .00 .00 .00 .00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.446E-03 4.8867</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bo (OVERALL)</td>
<td>11.00 .00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-.04876 .04306 .02824 .00000 .00000 .00000 .00000 U V W CT Z X Y</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>81.00 151.00 51.00 .00 .00 .00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.7950 58.0806 7.8967 90.0000105.8451 90.0000</td>
<td>CELL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PARAMETERS</td>
<td>91.00 101.00 111.00 .00 121.00 .00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.00000 .00000 .00000</td>
<td>PREF1 PREF2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R/RCFASYM</td>
<td>.00 .00 .00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.4493 -.0054 .0000</td>
<td>NA NB NC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(MIX_PARAMS)</td>
<td>61.00 141.00 .00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.0000 .0000 .0000</td>
<td>NA NB NC (HIGH SIDE)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.00 .00 .00</td>
<td>PEARSON</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASYM_FACTOR</td>
<td>.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2. Input file for calculation of powder diffraction pattern of interdigitated polymorph of n-decylammonium chloride from fractional coordinates reported by Schenk [1986]

C1ONCl 1986 Schenk Calculate diffraction pattern

<table>
<thead>
<tr>
<th>2</th>
<th>5</th>
<th>1</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>1</th>
<th>0</th>
<th>1</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.54050</td>
<td>1.54050</td>
<td>.00000</td>
<td>10.0000</td>
<td>8.0000</td>
<td>.9764</td>
<td>.00000</td>
<td>15.0000</td>
<td>.00000</td>
<td></td>
</tr>
<tr>
<td>.10</td>
<td>.90</td>
<td>.90</td>
<td>.90</td>
<td>2.0</td>
<td>.010</td>
<td>60.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.00000</td>
<td>.00000</td>
<td>.00000</td>
<td>.00000</td>
<td>1.0000</td>
<td>.00000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>000.0000</td>
<td>31.0000</td>
<td>121.0000</td>
<td>131.0000</td>
<td>141.0000</td>
<td>151.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

P 2 1

SPACE GROUP

C1 2 2 Cl .73350 .25000 -.03895 4.00000 1.00000 LBL M NTYP x y z B So
| .00000 | .00000 | .00000 | .00000 | .00000 |
| .00 | .00 | .00 | .00 | .00 |

C1 2 C .21480 .26200 .13080 4.00000 1.00000 LBL M NTYP x y z B So
| .00000 | .00000 | .00000 | .00000 | .00000 |
| .00 | .00 | .00 | .00 | .00 |

C2 2 C .42200 .26200 .19030 4.00000 1.00000 LBL M NTYP x y z B So
| .00000 | .00000 | .00000 | .00000 | .00000 |
| .00 | .00 | .00 | .00 | .00 |

C3 2 C .40400 .27300 .27980 4.00000 1.00000 LBL M NTYP x y z B So
| .00000 | .00000 | .00000 | .00000 | .00000 |
| .00 | .00 | .00 | .00 | .00 |

C4 2 C .60620 .20600 .34080 4.00000 1.00000 LBL M NTYP x y z B So
| .00000 | .00000 | .00000 | .00000 | .00000 |
| .00 | .00 | .00 | .00 | .00 |

C5 2 C .59650 .27500 .43210 4.00000 1.00000 LBL M NTYP x y z B So
| .00000 | .00000 | .00000 | .00000 | .00000 |
| .00 | .00 | .00 | .00 | .00 |

C6 2 C .79880 .20800 .48900 4.00000 1.00000 LBL M NTYP x y z B So
| .00000 | .00000 | .00000 | .00000 | .00000 |
| .00 | .00 | .00 | .00 | .00 |

C7 2 C .79390 .27700 .58220 4.00000 1.00000 LBL M NTYP x y z B So
| .00000 | .00000 | .00000 | .00000 | .00000 |
| .00 | .00 | .00 | .00 | .00 |

C8 2 C .99600 .20800 .63720 4.00000 1.00000 LBL M NTYP x y z B So
| .00000 | .00000 | .00000 | .00000 | .00000 |
| .00 | .00 | .00 | .00 | .00 |

C9 2 C 1.20000 .21100 .78250 4.00000 1.00000 LBL M NTYP x y z B So
| .00000 | .00000 | .00000 | .00000 | .00000 |
| .00 | .00 | .00 | .00 | .00 |

N 2 N .23500 .19100 .04380 4.00000 1.00000 LBL M NTYP x y z B So
| .00000 | .00000 | .00000 | .00000 | .00000 |
| .00 | .00 | .00 | .00 | .00 |

N 2 N .352E-03 4.0000 SCALE Bo(OVERALL)
| .5000 | .0000 | .0000 |

CELL PARAMETERS

| 11.00 | 111.00 |
| .00000 | .03634 |
| 191.00 | 321.00 |
| 5.6820 | 7.1660 |
| 51.00 | 71.00 |

PREF1 PREF2 R/RCFASYM

NA NB NC (MIX_PARAMS)
3. Input file for calculation of powder diffraction pattern of interdigitated polymorph of n-dodecylammonium chloride from fractional coordinates reported by Silver [1995]

C12NC1 1995 Silver

2 5 0 0 0 0 1 0 0 0 LINE 2.1

00111 10010 00000 00000 00000 00000 00000 00000 00000 00000 00000 00000 00000 00000

1.54050 1.54050 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000

P 21

SPACE GROUP

C1 2 CL 1.25930 .25000 -.53474 4.00000 1.00000 LBL M NTYP x y z B So
datawords
codewords
codewords
C1 2 C .81010 .26200 -.38350 4.00000 1.00000 LBL M NTYP x y z B So
datawords
codewords
codewords
C2 2 C .61350 .20250 -.33490 4.00000 1.00000 LBL M NTYP x y z B So
datawords
codewords
codewords
C3 2 C .64850 .26800 -.25440 4.00000 1.00000 LBL M NTYP x y z B So
datawords
codewords
codewords
C4 2 C .45460 .20970 -.20420 4.00000 1.00000 LBL M NTYP x y z B So
datawords
codewords
codewords
C5 2 C .48150 .27600 -.12370 4.00000 1.00000 LBL M NTYP x y z B So
datawords
codewords
codewords
C6 2 C .28740 .21060 -.07500 4.00000 1.00000 LBL M NTYP x y z B So
datawords
codewords
codewords
C7 2 C .30890 .27700 .00660 4.00000 1.00000 LBL M NTYP x y z B So
datawords
codewords
codewords
C8 2 C .11480 .21080 .05460 4.00000 1.00000 LBL M NTYP x y z B So
datawords
codewords
codewords
C9 2 C .11450 .27610 .13590 4.00000 1.00000 LBL M NTYP x y z B So
datawords
codewords
codewords
C10 2 C -.05940 .20760 .18400 4.00000 1.00000 LBL M NTYP x y z B So
datawords
codewords
codewords
C11 2 C -.04460 .27400 .26600 4.00000 1.00000 LBL M NTYP x y z B So
datawords
codewords
codewords
4. Input file for calculation of powder diffraction pattern of interdigitated polymorph of n-dodecylammonium bromide from fractional coordinates reported by Lunden [1974]