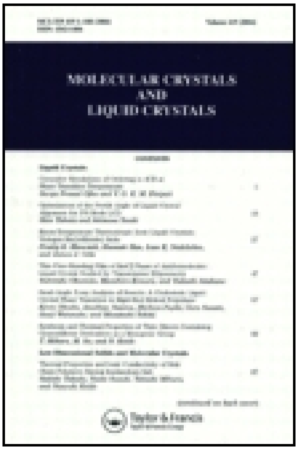

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PROBING THE PROPERTIES OF UREA INCLUSION COMPOUNDS

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Abstract The value of adopting a multiply-pronged experimental and computational approach in the study of organic solids is illustrated by summarizing some of our recent investigations of urea inclusion compounds containing diacyl peroxides or n-alkanes as the guest component. Structural and dynamic properties of these systems have been probed using single crystal X-ray diffraction, powder X-ray diffraction, ^{2}H nmr spectroscopy, and computer simulation (Monte Carlo methods).

INTRODUCTION

We are currently investigating several aspects of the chemistry and physics of solid inclusion compounds, with particular emphasis on those, such as urea and thiourea inclusion compounds as well as certain zeolitic materials, in which the "host" solid contains uni-directional tunnels. In part, our interest in these systems originates from a wider desire to compare the structural, dynamic, and chemical properties of organic molecules embedded within different crystalline environments, and to investigate how the properties of the molecule may be influenced by the structural characteristics, or other attributes, of its environment. Full details of our investigations have been[1-4], or will be, reported elsewhere. In this paper, we aim not to give a comprehensive account of these investigations, but rather to present an overview highlighting the approaches that can be used profitably to study various aspects of urea inclusion compounds. Urea inclusion compounds containing the following guest species (subsequently referred to by the abbreviations given) are discussed in this paper:

$CH_3.(CH_2)_6.(CO).O.O.(CO).(CH_2)_6.CH_3$	dioctanoyl peroxide (OP)
$CH_3.(CH_2)_9.(CO).O.O.(CO).(CH_2)_9.CH_3$	diundecanoyl peroxide (UP)
$CH_3.(CH_2)_{10}.(CO).O.O.(CO).(CH_2)_{10}.CH_3$	lauroyl peroxide (LP)
$Br.(CH_2)_5.(CO).O.O.(CO).(CH_2)_5.Br$	bis-(6-bromohexanoyl) peroxide (6-BrHP)
$CH_3.(CH_2)_{14}.CH_3$	n-hexadecane (HD)

STRUCTURAL ASPECTS OF (DIACYL PEROXIDE / UREA) INCLUSION COMPOUNDS : SINGLE CRYSTAL X-RAY DIFFRACTION STUDIES

General structural description of urea inclusion compounds

Our initial motivation for studying urea inclusion compounds containing diacyl peroxides (R.(CO).O.O.(CO).R') as the guest component was to investigate, primarily using esr spectroscopy, the contrasting photodecomposition behaviour of diacyl peroxides within different crystalline environments[5]. These inclusion compounds also exhibit many intriguing structural features[1,6], which became apparent only after carrying out photographic (rather than diffractometric) single crystal X-ray diffraction experiments. The value of conventional diffractometric methods is, in fact, severely limited, at least in the first instance, for elucidating the intricate structural details of urea inclusion compounds.

We begin by summarizing the general structural features of urea inclusion compounds[1,7]. Within these crystals, the urea molecules pack in an extensively hydrogen-bonded arrangement (Figure 1) containing linear, parallel, non-intersecting channels (tunnels) within which the guest molecules are located. The structural periodicities of the host (urea) and guest molecules are generally incommensurate along the channel axis, and it is therefore convenient to consider each single crystal to be composed of

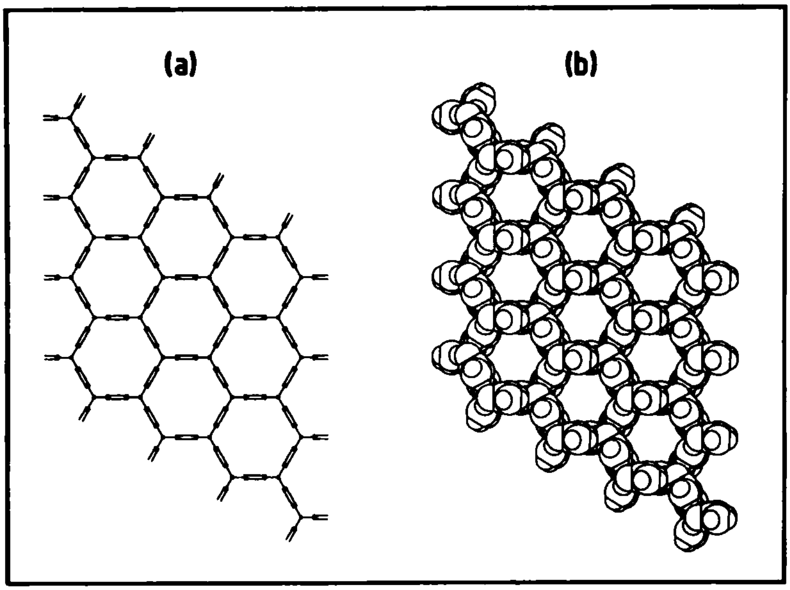

FIGURE 1 Two representations, showing 9 complete channels, of the basic host structure in urea inclusion compounds, viewed along the channel axis. Atomic radii are zero in (a) whereas conventional van der Waals radii are represented in (b). Space group $P6_122$; distance between centres of adjacent channels ≈ 8.22Å.

distinguishable, although not independent, host and guest substructures. The host substructure is best considered in terms of an incommensurately modulated "basic host structure". The basic host structure possesses 3-dimensional periodicity, and can be treated using conventional crystallographic principles. The incommensurate modulation describes structural perturbations to the basic structure which arise from host-guest interaction. Similarly, the guest substructure should be considered in terms of a "basic guest structure" which experiences an incommensurate modulation mediated by the host substructure.

On transforming this structural description to reciprocal space, it is clear that there are two separate diffraction patterns, designated the "h" and "g" diffraction patterns. The "h" diffraction pattern arises from diffraction by the basic host structure (and the incommensurate modulation of the guest substructure), whereas the "g" diffraction pattern arises from diffraction by the basic guest structure (and the incommensurate modulation of the host substructure). Additional complexity arises when there is more than one orientationally distinct domain of the basic guest structure (giving rise to several identical but orientationally distinct "g" diffraction patterns), and when different regions of the crystal contain different degrees of guest molecule ordering. To derive a detailed understanding of these structural features, it is essential, at least in the first instance, to use photographic single crystal X-ray diffraction methods in preference to diffractometric methods.

Structural features of the guest species in {diacyl peroxide/urea} inclusion compounds

For a number of reasons, devolving largely upon the mobility of the guest species under ambient conditions, it has not proven possible to determine the basic guest structure, in the conventional sense, for any of the urea inclusion compounds studied. Substantial information concerning the average periodicities of these basic guest structures, and their orientational relationships with respect to the host, has, however, been deduced from room temperature photographic single crystal X-ray diffraction experiments[1,6].

For {OP/urea}, {UP/urea} and {LP/urea}, the basic guest structure is monoclinic (probable space group C2) and there are six domains with distinguishable X-ray diffraction patterns. The relative packing of guest molecules is the same in each domain, and the different domains are related by 60° rotation about the channel axis. For each of these compounds, the offset between the "heights" of the guest molecules in adjacent channels is the same (~4.6Å) within experimental error, suggesting that the relative interchannel packing of guest molecules is controlled by a property of the diacyl peroxide group alone. In contrast to these urea inclusion compounds of unsubstituted diacyl peroxides, {6-BrHP/urea} exhibits no extensive 3-dimensional guest molecule ordering.

STUDIES OF A PHASE TRANSITION IN {n-HEXADECANE/UREA}

Introduction

Specific heat capacity measurements[8] suggest that {n-alkane/urea} inclusion compounds undergo a phase transition at a temperature which depends upon the identity of the guest molecule, and for {HD/urea} the transition occurs at about 150K. We have considered two aspects of this phase transition in {HD/urea}:

(i) alterations in the structural characteristics of the host, probed using powder X-ray diffractometry.

(ii) changes in the motional behaviour of the guest molecules, investigated by ^{2}H nmr spectroscopy.

Powder X-ray diffraction studies of {n-hexadecane/urea}

Powder X-ray diffraction studies of {HD/urea} have been carried out[1,9] between 296.3K and 46.2K (see Figure 2(a)). The significant change in the diffractogram between 150.5K and 148.7K indicates that the symmetry of the average basic host structure changes from hexagonal in the high temperature phase (space group $P6_122$) to orthorhombic in the low temperature phase (probable space group $P2_12_12_1$). This assessment of the transition temperature is in good agreement with measurements from alternative experimental approaches[8,10-12] (see also the ^{2}H nmr results below), and our interpretation of the structural change associated with the transition confirms earlier speculations[13] based on single crystal X-ray diffraction investigations. No satisfactory determination of the basic host structure within the low temperature phase has been reported, and since multiple crystal twinning is thought to accompany the phase transition on passing from the high temperature to the low temperature phase, powder X-ray diffraction represents a more viable route to this information than single crystal X-ray diffraction. Structure refinement from the powder X-ray diffraction data collected at 119.7K is in progress using the Rietveld profile refinement method.

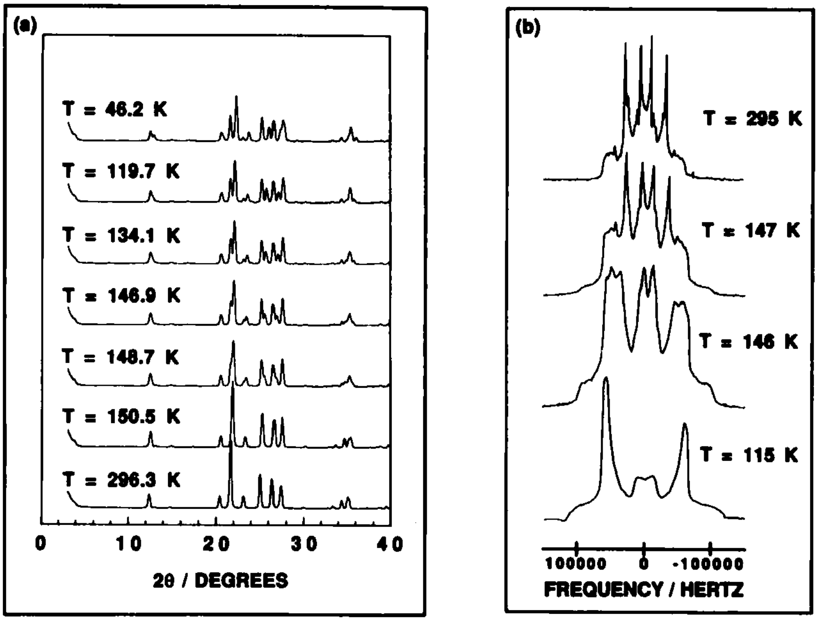

FIGURE 2 (a) Powder X-ray diffractograms (CuK$_\alpha$ radiation) recorded for {HD/urea}.
(b) ^{2}H nmr spectra recorded for a "static", polycrystalline sample of {d$_{34}$-HD/urea}.

^{2}H nmr spectroscopic investigations of {n-hexadecane/urea}

Although many experimental techniques can be used to probe molecular motion within organic solids (several having been applied previously to study guest motion within urea inclusion compounds), ^{2}H nmr spectroscopy has emerged in recent years as a particularly powerful method in view of the detailed mechanistic information that it can reveal. We illustrate this fact with reference to our variable-temperature ^{2}H nmr investigations of perdeuterated n-hexadecane (d$_{34}$-HD) within its urea inclusion compound[1,3]. From the spectra shown in Figure 2(b), motional information has been deduced over a wide temperature range, and at room temperature, for example, the dynamic properties of the d$_{34}$-HD molecule are as follows:

(i) 60° jumps about the long molecular axis (which is, on average, coincident with the channel axis),

(ii) torsional libration (with approximate amplitude ±25°) about the penultimate C–C bond,

(iii) rapid rotation of the CD_3 group about the $C-CD_3$ bond.

The dramatic change in the ^2H nmr spectrum between 146K and 147K suggests that the phase transition in {HD/urea} is associated with an abrupt discontinuity in the motional freedom of the HD molecule, although there is nevertheless appreciable motion even below the phase transition temperature.

MONTE CARLO SIMULATION STUDIES OF UREA INCLUSION COMPOUNDS

Both Monte Carlo (MC) and molecular dynamics (MD) simulation techniques are now being applied extensively to investigate solid state problems, and notable successes have been reported recently in the study organic molecules included within zeolitic hosts[14,15]. The prospects for the {organic guest/organic host} systems are also encouraging, as we now illustrate by summarizing the results our MC investigations of the following problems concerning urea inclusion compounds[1,16]:

A The response of the "empty" host substructure following removal of the guest species from a urea inclusion compound.

B The structural properties of the guest molecules in {HD/urea}, assuming a rigid host framework and conformationally invariant guest molecules.

All simulations were conducted under conditions of constant temperature and pressure (i.e. in the isothermal-isobaric ensemble).

The results of simulation A verify earlier experimental studies[17] which suggest that, at room temperature and atmospheric pressure, the "empty" urea host framework is unstable. Simulation B has revealed important information (at a variety of different temperatures and pressures) relating to: (i) local structural aspects of the guest substructure in {HD/urea}, and (ii) energetic aspects of host-guest and guest-guest interactions in this system.

It is clear that, provided appropriate intermolecular potential energy parameterizations are available or can be readily derived, computer simulation will play an increasingly important role in the future investigation of a diverse array of problems relating to organic inclusion compounds. MD methods should prove particularly informative since they are able to reveal detailed information on time-dependent properties which, inter alia, can be compared directly to dynamic information obtained experimentally.

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