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Molecules in Motion: a Study in the Synergy of X-ray Diffraction and Solid State NMR*

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The Fourier transform of the X-ray diffraction pattern of a crystal is the electron density of the crystal averaged over space and time. In the determination of the structure of a crystal this electron density is modeled by a set of spheres of electron density representing the atoms together with a »smearing function«, the atomic displacement parameters, representing the motion (translation and libration) of those atoms. Studies of the deuterium and ^{13}C NMR of these solids show that these XRD parameters give a less than full picture of the motional behavior in crystals. In particular XRD parameters do not give information about infrequent activated processes in the crystal or about some motional behavior related to phase changes. A number of examples of the synergy of XRD and solid state NMR will be given. These examples include phenyl ring flips in phenoxypenicillin salts, whole molecule rotations in *ansa*-titanocene halides, guest molecule tumbling, spins and flips in thiourea clathrates cycloheptane and cyclooctane guests, cation flips and spins in thiourea pyridinium halides, wobbles, spins and phase changes in the deoxycholic acid ferrocene clathrate and motion, phase changes and chiral selectivity in the deoxycholic acid clathrates with *R* and *S* camphor, with reference to how solid state NMR gives information about the mechanism of the phase change.

Key words: ^{13}C CP MAS NMR, ^{2}H NMR, $(deoxycholic\ acid)_2$: ferrocene, $(DCA)_2$: *RS*-camphor, $(DCA)_2$: *R*-camphor, $(DCA)_2$: *S*-camphor, inclusion compounds.

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INTRODUCTION

The structure of a molecular crystal is usually thought of as a rather rigid system. The molecules have a fixed orientation and conformation. The atoms within the molecule execute small amplitude vibrations and the molecule as a whole executes a small amplitude libration. This concept of the crystal is a result of the way the diffraction pattern is modelled together with the timescale of the experiment. The Fourier transform of the X-ray diffraction (XRD) pattern of a crystal is the electron density averaged over space and time. In general this transformation cannot be performed directly because we only have knowledge of the position and intensity of the X-ray reflections and are ignorant of the phases. To perform the transformation we obtain a set of approximate phases from statistical relationships within the intensity data (direct methods) and compute an approximation to the electron density. This is then modelled as a set of spheres located at local maxima in electron density together with a smearing function, the temperature factor or atomic displacement parameters (ADP). The locations of the spheres of electron density and temperature factors are then refined until a best fit with the observed intensities is obtained. At the point of best fit the positions of the centres of electron density are a very good approximation to the positions of the atomic nuclei. In the familiar ORTEP (Oak Ridge Thermal Ellipsoid Plot) diagram the temperature parameters are represented in real space as an ellipsoidal surface for each atom and are often thought as representing a volume swept out by the motion of that atom. The temperature factors may be interpreted in terms of the principal vibrational modes of the crystal or more usually the translational and librational motions of the molecules within the crystal. They can be used to compute infrared and Raman spectra or bond length corrections but more usually they are used intuitively to indicate motion or disorder. Thus the ORTEP diagram of the non-coplanar tetraphenylene[1] would be interpreted as that of a molecule showing a very substantial librational motion centred to the left of the centre of gravity of the molecule (Fig. 2 in Ref. 1) Molecular translational and librational motions have frequencies comparable to the time scale for the interaction of X-rays with matter. Other less frequent motional events will not be recorded by XRD because they are slow on the X-ray time scale and make only minimal contribution to the average electron density.

The alternative major technique for the determination of molecular structure is NMR spectroscopy. Normally a solution method, NMR like XRD is dependent on the electron density distribution in the molecule and like XRD it provides information about molecular structure and molecular motion. However NMR operates on a time scale between 1 and 10^{12} s^{-1} complementary to that of XRD. Just as solution NMR enables us to study motional

events in solution, solid state NMR presents an alternative technique for the observation of molecular motion in the solid state. Additionally solid state NMR is responsive to structure up to *ca.* 10 Å from the target nucleus, is sensitive to crystallographic details such as unit cell content and is suitable for amorphous materials. The sensitivity to short range structure contrasts with XRD which depends on an averaging over many thousand unit cells.

MOLECULAR MOTION IN THE SOLID STATE: EXAMPLES OF XRD AND NMR SYNERGY

Phenyl Ring Flips in Phenoxypenicillin Salts

One low frequency molecular motion that is commonly observed by solution NMR is the 180° flip of a phenyl ring in phenylalanine and tyrosine residues in proteins. This proceeds by an activated process mechanism and occurs even when there is, apparently, insufficient space for the phenyl group to rotate. Ring flips similar to those observed in proteins can be found in the solid state, for example in crystals of the alkali metal salts of phenoxypenicillin[2] (PenV). The caesium salt[3] is typical. In the crystal structure the metal cations form sheets and are coordinated by the penam oxygen atoms to form a sandwich with the phenyl groups on the outside.[3] The ADP ellipsoids indicate a pendulum like motion of the phenyl groups. The aromatic region of the solid state variable temperature (VT) ^{13}C CP MAS (cross-polarisation magic angle spinning) NMR spectra gives a different picture.[3] In the crystal the C3' and C5' and C2' and C6' are two non-equivalent pairs of atoms. ^{13}C CP MAS NMR spectra at low temperature separate signals for C2' and C6' (the C3' and C5' signals coincidentally overlap). As the temperature is increased the signals broaden and coalesce (at 237 K), shrink to nothing (at 274 K) then reappear and sharpen (at 331 K). This corresponds to a two fold exchange of C2' and C6' and of C3' and C5' the exchange rate being equal to the de-coupling frequency (70 kHz) at about 274 K. These spectra are interpreted as a phenyl ring flip which has a frequency of about 100 kHz at room temperature. It can be shown to be an activated process with an activation energy of (72 ± 10) kJ mol^{-1}. Surprisingly not only is there no XRD evidence for the ring flip but there is no space in the structure as seen by X-rays for the phenyl ring to rotate through 180°.[3]

Molecule Rotations in ansa*-Titanocene Halides*

Whole molecules may undergo a similar rotational motion in the crystal. This we found in family of *ansa*-titanocenes dihalides.[4] There are two mole-

cules of the *ansa*-titanocene dichloride in the asymmetric unit. The molecules are packed in layers each layer containing only one crystallographically distinct molecule. The structure is well refined. The ADP ellipsoids are small and approximately spherical indicating a lack of disorder or unusual thermal motion. The molecule is potentially chiral and in solution can be shown to undergo a fast enantiomeric interchange.[4]

In contrast although solid state ^{13}C CP MAS NMR spectra, in the temperature range 200–380 K show resonance multiplicities consistent with the crystallographically determined asymmetric units, 1D and 2D magnetization transfer experiments below 300 K and line shape simulations of exchange-broadening phenomena all indicate a pair-wise exchange process for one molecule in the asymmetric unit whilst the other molecule remains rigid. The measured Arrhenius activation barrier, E_a = 86 kJ mol^{-1} for the dynamic molecule. The joint interpretation of the NMR and X-ray data indicates that the dynamic processes detected for this molecule by NMR are not the expected enantiomeric exchange process. This process is observed to be facile in solution but would lead to disorder in the solid.[4] Both the NMR and X-ray data are, however, consistent with a hypothesis that a 180° reorientation about the pseudo-C_2 axis, bisecting the X–Ti–X interbond angle, occurs in the crystal concomitant with a small polytopal relaxation about the metal centre. This process averages carbon atoms in a pair-wise manner, but leads to no atomic positional disorder and it averages the ^{2}H electrical field gradient and ^{13}C chemical shift anisotropy (CSA) tensors only slightly. The results from the ^{13}C studies are consistent with those from ^{2}H solid state NMR.[4] The motion constitutes an interesting dynamic mode of a molecular crystal, which is intermediate between the well-established examples of the effectively isotropic overall molecular re-orientational disorder characteristic of a plastically crystalline phase, and the disorder or fluxionality of specific groups or moieties within a molecule.

Guest Molecule Tumbling, Spins and Flips in Thiourea Clathrates

The recognition that molecules in a crystal may not be equally mobile finds an extreme in the case of the molecular complex with a rigid guest structure and a mobile host. This situation is well exemplified by the thiourea clathrates. Unfortunately, X-ray crystallographic studies are often difficult or ambiguous because guest and host are incommensurate. The thiourea cycloheptane (TC7), and cyclooctane (TC8) inclusion compounds[5] and the thiourea pyridinium halide salts[6] provide interesting examples that are commensurate solids. There are extensive thermodynamic studies on TC7, TC8 by Cope, Gannon and Parsonage.[7] The heat capacity curve for TC8 indicates four possible phases with rather broad second order phase changes

centred around 266 and 241 K and a much sharper change at 187 K.[7] These changes were found to take place with retention of crystallinity and the diffraction patterns were observed at 293, 250, 210 and 150 K. At room temperature, the cyclooctane adduct exhibits the classical thiourea adduct rhombohedral lattice (space group $R\bar{3}c$). In these structures, the well resolved host thiourea structure is composed of one-dimensional non-intersecting channels running along the *c*-axis (hexagonal setting). The guest molecules, located in the center of the channel, are highly disordered and may be modelled as a spherical shell of electron density. Lowering temperature to 250 K gives a second hexagonal phase with the *a*-axis doubled. The additional reflections are weak and the changes (which we have so far failed to model) from the room temperature phase appear to be rather subtle. Further cooling to 210 K leads to a monoclinic phase resulting from the distortion of the room temperature lattice. There is one guest molecule site in the asymmetric unit. The guest molecules can be located but still have some degrees of disorder. A successful refinement has been performed with a model involving two cyclooctane molecules of the same conformation but different orientations at the molecular site. Below 200 K the axis parallel to the guest channels is doubled leading to a new phase with two independent cyclooctane sites occupied by molecules having the same conformation, but two different orientations.[5]

Variable temperature solid state ^{13}C NMR spectra have been recorded over the temperature range 133–293 K. There are two maxima: one, very weak, at about 182 ppm due to the thiourea and the other at about 27.7 ppm for the cyclooctane carbon atoms. At 293 K the latter is very sharp, similar to that observed in a liquid. So much so that it is sharp without MAS. This is attributed to the very rapid tumbling of the cyclooctane in the thiourea channels. It also suggests that it would be improper to attempt to model the individual atomic positions for the cyclooctane. What is surprising is first that there is no specific evidence for the three phase changes in the NMR. Secondly, even at 133 K when the XRD indicates a fully ordered structure, the rate of exchange of the cyclooctane carbon atoms is so fast that a sharp signal is obtained without cross polarization using a one pulse sequence followed by high-powered proton decoupling (PDA pulse sequence).

Cation Spins and Flips in Thiourea Piridinium Halides

The thiourea pyridinium halide inclusion compounds[6] present a rather different story, which is well illustrated by our studies of the bromide. As previously reported by Trutter and Vickery[8] the bromide, at room temperature forms orthorhombic crystals in space group *Cmcm*. The pyridinium cation is disordered in the square cross section thiourea channels. On cooling,

the bromide undergoes a phase change between 170 and 165 K to a partially ordered form in space group $Cmc2_1$ with the a-axis tripled.[6] A second phase change occurs between 140 and 150 K to a fully ordered phase in space group $P2_1cn$ and cell dimensions approximately the same as the room temperature form.[6] The phase transitions have also been studied by VT ^{2}H NMR of the perdeuteropyridinium salts. These data have been compared with the XRD data and with models for the motion of the pyridinium cation. Below 230 K the VT ^{2}H NMR spectra can be simulated if it is assumed that there is an in-plane librational motion of amplitude ϕ combined with an out of plane wobble of amplitude β. There appears to be no change in the motional character of the pyridinium cation at either of the two phase-changes even though the only major contributor to the phase change is the degree of ordering of the cation.

Wobbles, Spins and Phase Changes in the Deoxycholic Acid Ferrocene Clathrate

A motion of libration plus wobble is also found for the guest ferrocene in the deoxycholic acid (DCA) inclusion complex $(DCA)_2$: ferrocene. The structure of this complex was first reported by Miki, Kasai, Tsutsumi, Miyata, Takemoto[9] who claimed that it was orthorhombic space group $P22_12_1$ with one DCA molecule in the asymmetric unit and the ferrocene on the two-fold axis. The DCA molecules form hydrogen bonded sheets with the ferrocene in channels between these sheets. The crystallographic axis parallel to the ferrocene containing channels is 7.127 Å. The ^{13}C CP MAS NMR spectra are given in Figure 1 with particular emphasis on the methyl region (C18, C19 and C21). These spectra suggest two crystallographically distinct DCA molecules in the unit cell at room temperature.[10] On heating they become increasingly similar, until beyond *ca.* 345 K only one type of DCA molecule per unit cell is indicated. Repeating the room temperature single crystal XRD experiment[11] we found that there were a very substantial number of weak reflections present that required a 14.11 Å channel axis and the space group $P2_12_12_1$. The subsequent structure analysis showed that the DCA sheets had corrugations parallel to the b axis, Figure 2a. On heating above 320 K these reflections lost intensity and had vanished by 360 K. The high temperature phase had the structure previously proposed for the room temperature phase. Thus it appears that these crystals undergo a 'gradual' phase transition above ambient temperature 'completed' by *ca.* 360 K and the low and high temperature structures are compared in Figure 2.

The phase transition is characterised using ^{13}C CP MAS NMR spectroscopy, Figure 1. The transition, although most clearly observed in the positions of the deoxycholic acid molecules, is largely dominated by the dynamic

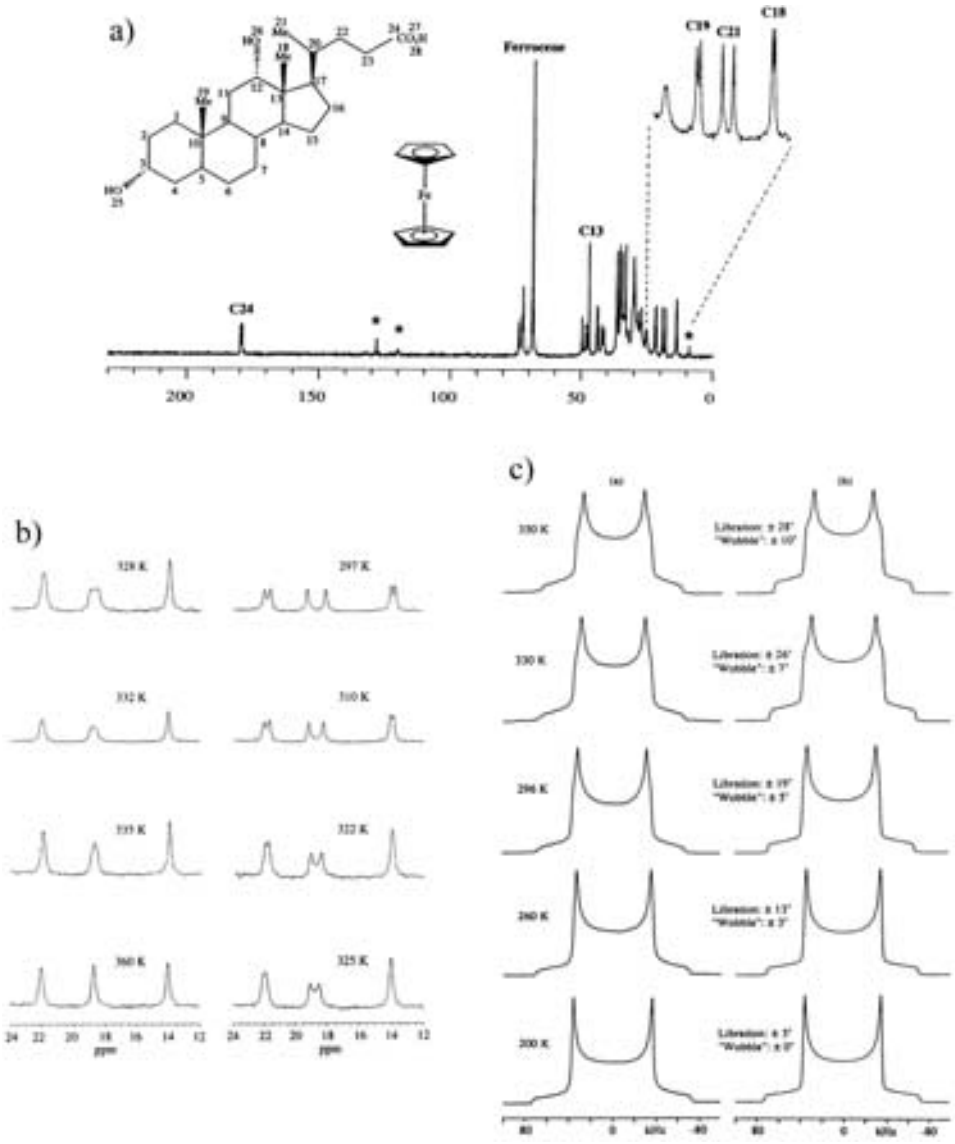

Figure 1. (a) The complete ^{13}C CP MAS NMR spectrum for $(DCA)_2$: ferrocene at 297 K together with the structural formula and atom numbering (* indicates a spinning side band). (b) The methyl region of the ^{13}C CP MAS NMR spectra of $(DCA)_2$: ferrocene at selected temperatures. (c) Experimental and simulated solid state deuterium NMR of the complex formed using perdeuterated ferrocene together with simulations based on a libration and wobble of the ferrocene molecule.

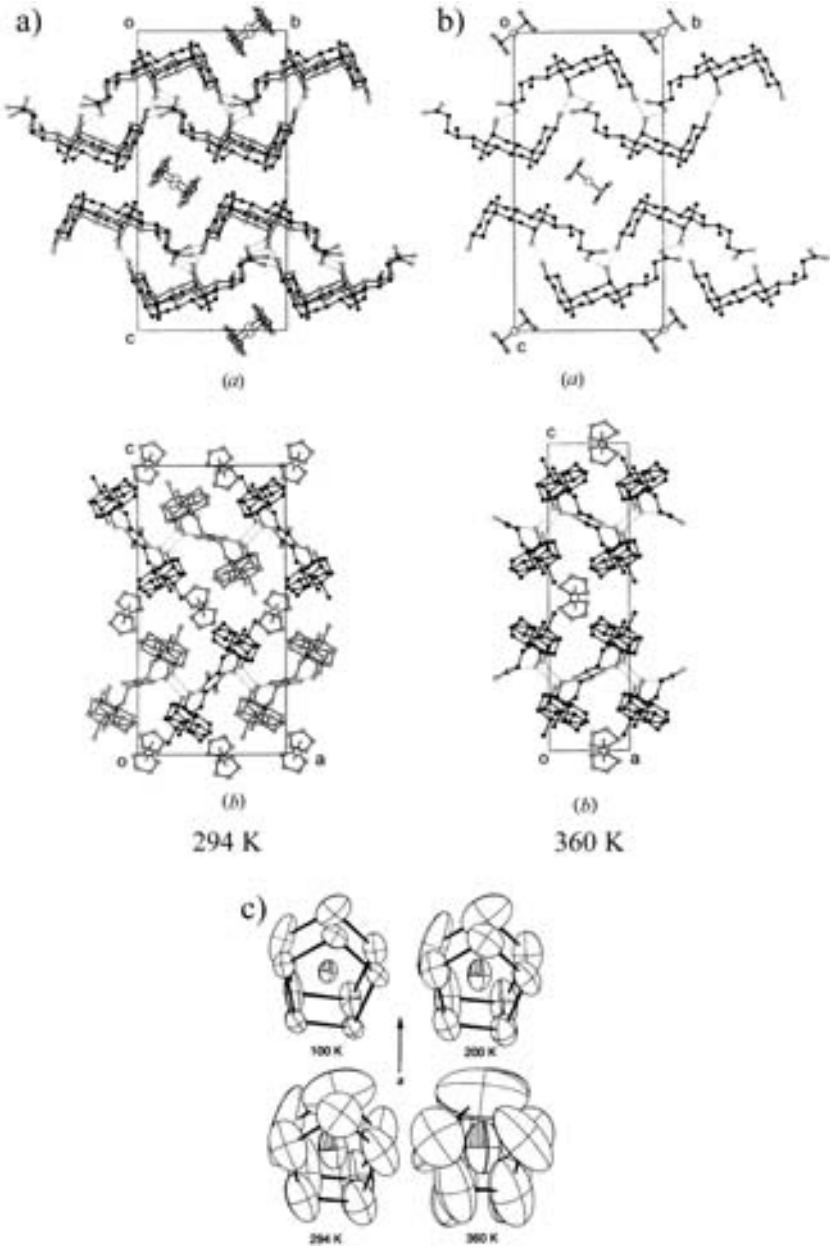

Figure 2. The crystal structure of $(DCA)_2$: ferrocene at 294 K (a) and at 360 K (b) viewed along *a*- and *b*-axes. The hydrogen bonds are represented by dotted lines. Thermal ellipsoids of the ferrocene guest molecules of $(DCA)_2$: ferrocene (c) at 100 K, 200 K, 294 K and 360 K showing the shape and direction of the thermal ellipsoids reflect the postulated 'wobble' of the ferrocene.

behaviour of the included guest ferrocene molecules. The mechanistic nature of the phase change can be obtained from the NMR spectra. Figure 3 gives a schematic NMR spectra representing the progress of a transformation of a system from a phase with two distinct environments for a spin to one with a single environment for the spin. In (a) there is a gradual crystallographic change from one phase to the other, whereas for (b) there is a nucleation and growth of the product phase within the original phase. The experimental spectra clearly correspond to (a) and not (b), Figure 1. Fortunately, perdeuteroferrocene is ready available and the variable temperature ^{2}H solid state NMR have been observed.

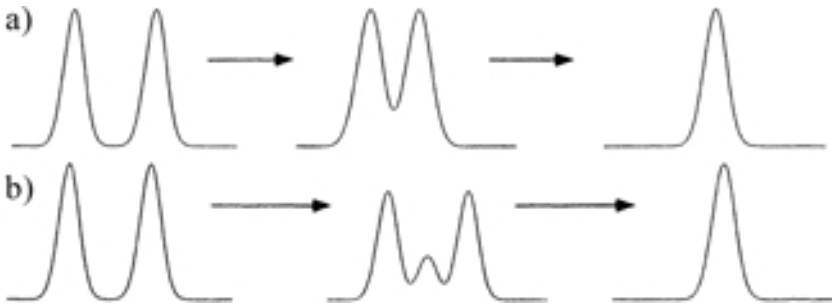

Figure 3. Schematic NMR spectra representing the progress of a transformation of a system from a phase with two distinct environments for a spin to one with a single environment for the spin, (a) where there is a gradual crystallographic change from one phase to the other, and (b) where there is a nucleation and growth of the product phase within the original phase.

Figure 1 affords us some information about the motion of the ferrocene. These spectra are readily simulated if a libration about the five-fold axis is combined with a wobble of that axis. The crystal structure of $(DCA)_2$: ferrocene has been determined at 360, 294, 200 and 100 K. We can now make more sense of the ADP ellipsoids in Figure 2 if it is assumed that the wobble is centred on the upper ring so that the larger amplitude of motion is associated with the lower ring. On this assumption a simple model in which the limits of the wobble are defined by the foci of the ADP ellipsoids of the lower ring, suggests angles of wobble of 11.8, 8.3, 7.0 and 5.5° at 293, 248, 198 and 148 K respectively.

It is fortuitous that the ferrocene in the ferrocene DCA complex has a molecular 2-fold axis that coincides with the crystallographic 2-fold axis. Consider a DCA complex, which has a high temperature form in space group $P22_12_1$ with a guest molecule without any molecular symmetry. The guest

will be disordered about the 2-fold axis. There are three ways in which the system may order. The *a* axis may double to give ordering in the orthorhombic space group $P2_12_12_1$ with a 2-fold screw axis along *a*. Or the 2-fold axis may be lost in which case the crystals become monoclinic with either *b*, $P12_11$, or *c*, $P112_1$, the unique axis. Typically the unit cell dimensions are unchanged and the β angle is very close to 90°.

Motion, Phase Changes and Chiral Selectivity in the Deoxycholic Acid Clathrates with Camphor

The ferrocene molecule is roughly spherical and other roughly spherical guests might be expected to behave in a similar manner so the thermal behaviour of the 2:1 inclusion compounds of deoxycholic acid (DCA) with camphor[12] were examined. Since DCA is chiral the channels are chiral so that the chiral guest molecule camphor has an added interest. The crystal structures of the 1*R*- and 1*S*-camphor complexes have been reported and have the same unit cell as the high temperature form of the $(DCA)_2$: ferrocene complex. The expectation was therefore that these complexes would have a low temperature form isostructural with the low temperature form of $(DCA)_2$: ferrocene. The complete ^{13}C CP MAS NMR spectrum for $(DCA)_2$: 1*R*-camphor at room temperature, Figure 4, serves to confirm the published structure and the detail of the methyl region of the DCA spectrum indicates a phase change at about 242 K to a form with two DCA molecules in the asymmetric unit. The XRD patterns also suggest a phase change at about 242 K but it is from an orthorhombic high temperature form to a monoclinic low temperature form in space group $P2_1$ with the same unit cell lengths and a β angle of 91°, Figure 5 (b). The 1*R*-camphor is ordered and the DCA layers are differentiated by the orientation of the 1*R*-camphor in the cavities (filled and open circles in Figure 5).

On examination of the $(DCA)_2$: 1*S*-camphor complex by XRD no phase change was found above 100 K and there was little evidence for a phase change above 20 K. Solid state NMR afforded no evidence of a phase change above 200 K the low temperature limit of the spectrometer probe that we were using at the time.

The $(DCA)_2$: 1(*RS*)-camphor complexes containing 1*R*- and 1*S*-camphor in a wide range of enantiomeric ratios have been investigated by combination of single-crystal XRD in the temperature range 100–325 K and solid state ^{13}C NMR between 297 K and 200 K, Figure 7. Both techniques show that an order-disorder phase transition occurs between 250 K and 240 K for the pure 1*R*-camphor complex. The onset temperature decreases and temperature duration of the phase change increases as the 1*S* enantiomer is introduced reaching 180 K for the 1:1 racemate. When larger proportions of

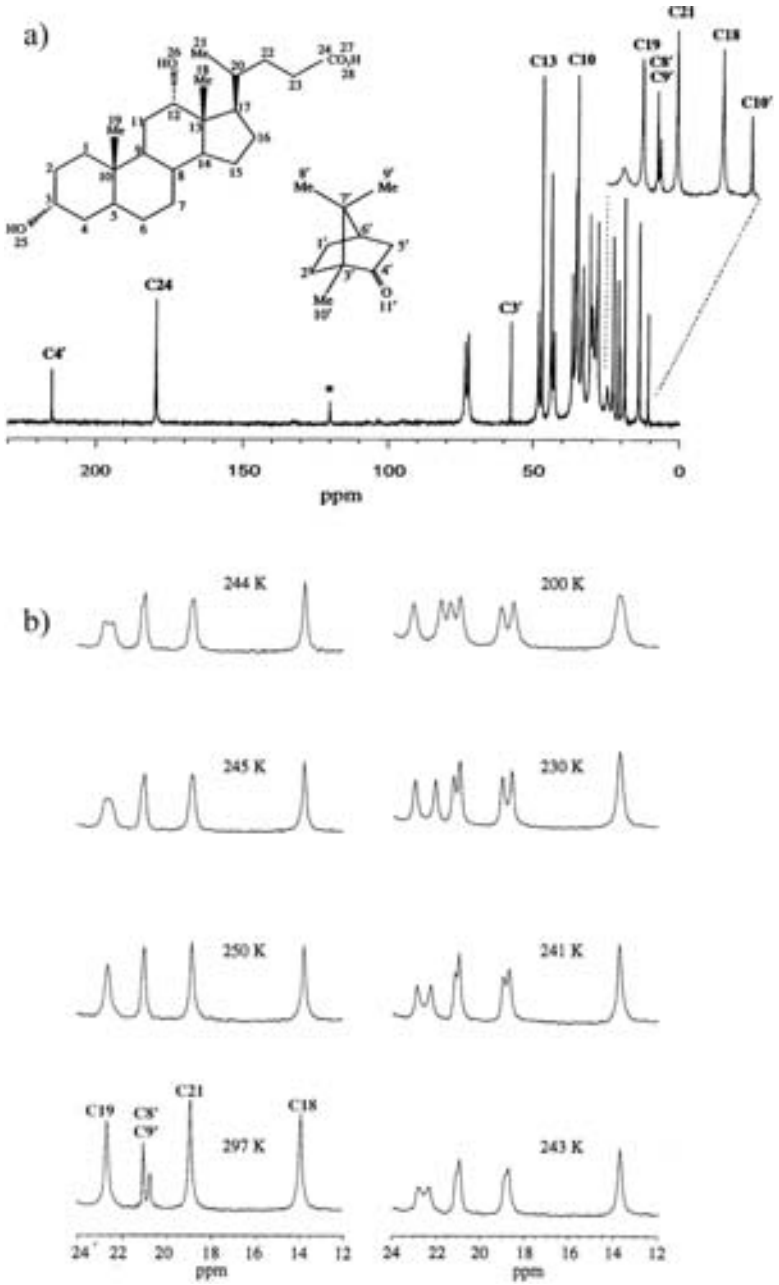

Figure 4. (a) The complete ^{13}C CP MAS NMR spectrum for $(DCA)_2$: 1*R*-camphor at 297 K together with the structural formula and atom numbering (* indicates a spinning side band). (b) The methyl region of the ^{13}C CP MAS NMR spectra of $(DCA)_2$: 1*R*-camphor at selected temperatures.

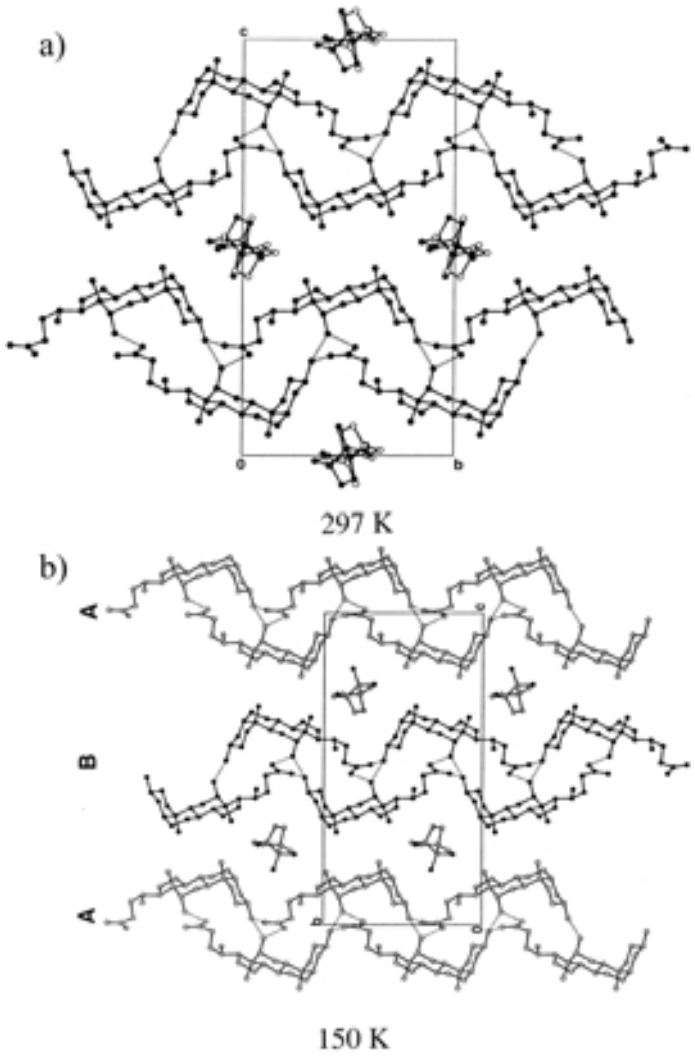

Figure 5. The high (a) and low (b) temperature phases of the $(DCA)_2$: 1*R*-camphor. The high temperature phase is orthorhombic and isostructural with the high temperature of $(DCA)_2$: ferrocene but the low temperature phase is monoclinic.

the 1*S* enantiomer were introduced there was no recordable phase change above 100 K. At room temperature, the crystal structure of the inclusion compound is orthorhombic $P22_12_1$ for all enantiomeric ratios. When both *R* and *S* guests are present there is a double disorder, first that introduced by the crystallographic 2-fold axis then that due to the possibility that each guest site can be occupied by an *R* or an *S* molecule in the appropriate enan-

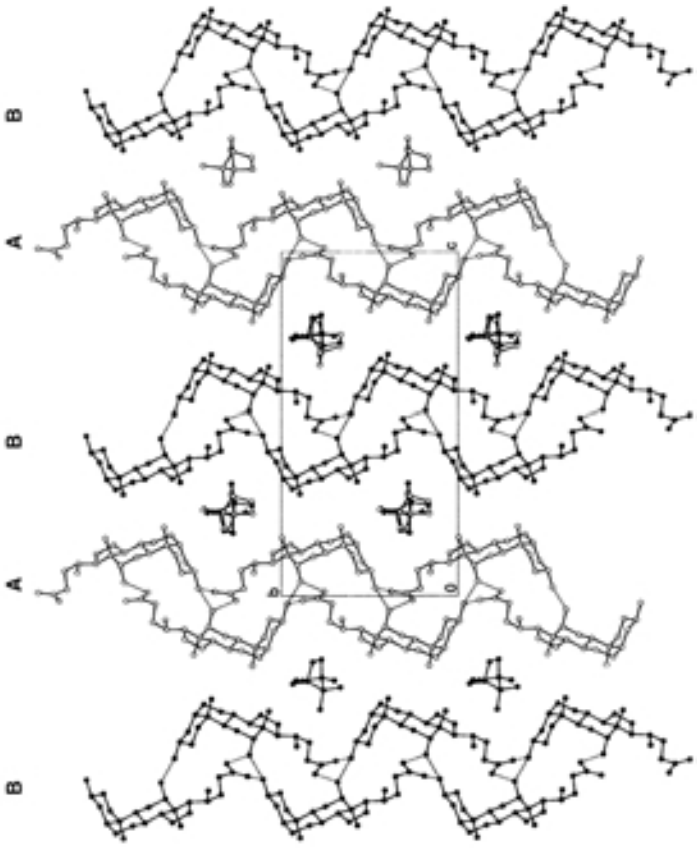

Figure 6. The low temperature monoclinic phase of $(DCA)_2$: (*RS*)-camphor; the two enantiomers of camphor are disordered at the crystal site however in the topmost and lowest channels in the diagram the orientations of the individual enantiomers can be seen. The topmost channel shows the orientation of the (*S*)-camphor (open circles) and the bottom channel the (*R*)-camphor (filled circles).

tiomeric ratio. In each case when a phase transition is observed, the low temperature phase is monoclinic as it is for the pure *R* complex. From the XRD data for the (*RS*) 50:50 complex at 100 K it is possible to locate both the *R* and the *S* camphor molecules, Figure 6. The 1*R*-camphor is shown with filled circles and is in the same orientation as in the pure 1*R*-camphor complex. The 1*S*-camphor, open circles is rotated approximately 90° from the 1*R* position.

The onset and completion temperatures for the phase change from the high temperature orthorhombic $P22_12_1$ to the low temperature monoclinic $P12_11$ for $(DCA)_2$: 1(*RS*)-camphor complexes with various enantiomeric ra-

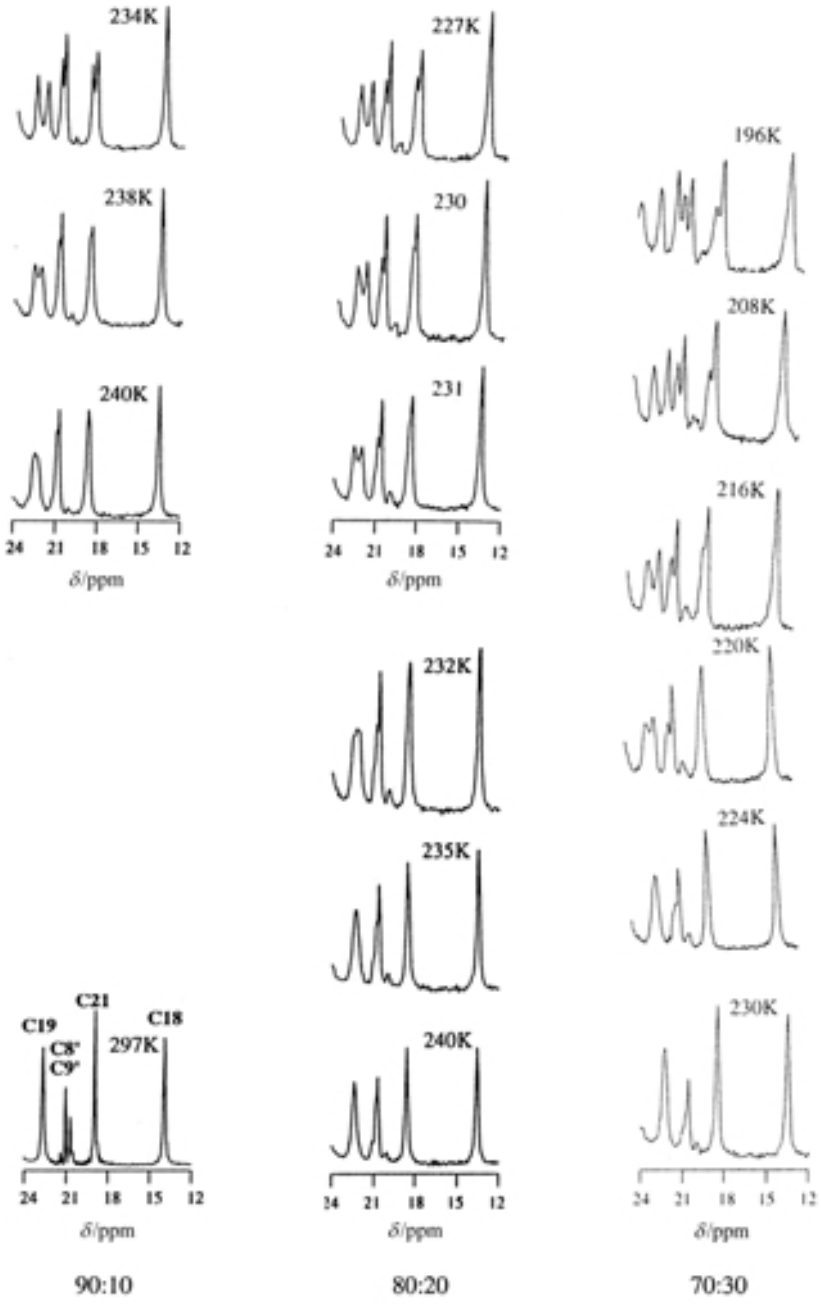

Figure 7. The methyl region of the ^{13}C CP/MAS NMR spectra of $(DCA)_2$: (*RS*)-camphor at selected temperatures with *R*:*S* ratios of 90:10, 80:20, 70:30 show the different temperatures of onset of the order/disorder phase transition.

TABLE I

$(DCA)_2$: 1(*RS*)-camphor complexes. Phase change from the high temperature orthorhombic $P22_12_1$ to the low temperature monoclinic $P12_11$

	NMR		XRD	
R:S	Onset/K	Complete/K	Onset/K	Complete/K
1:0	246	241	245	230
90:10	238	227		
80:20	231	218		
70:30	222	208	208	195
50:50			180	175
30:70			Yes, below 180 K	
0:1			Below 80 K if at all	

tios of camphor are given in Table 1, The ^{13}C CP MAS NMR spectra for various enantiomeric ratios are given in Figure 7 and the variation of β angle with temperature for the 70:30 *R*:*S* ratio complex is shown in Figure 8. Both XRD and NMR indicate that these phase changes have the characteristics of a second order phase transition. From the NMR experiments, the phase change was found to be induced by the dynamic behaviour of the 1*R*-camphor guest molecules.

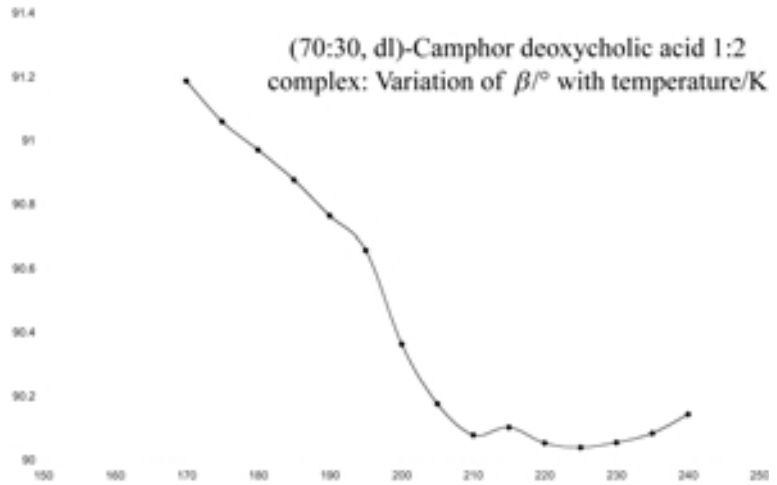

Figure 8. The variation with temperature of the monoclinic β angle of the $(DCA)_2$: (70:30, *R*:*S*)-camphor complex. The measurements were obtained using a Kappa ccd diffractometer and their interpretation assumed triclinic symmetry.

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SAŽETAK

Molekule u gibanju: studija sinergije difrakcije X-zrakâ i NMR krutinâ

Keith Prout

Fourierovom transformacijom röntgenske difrakcijske slike kristala dobiva se elektronska gustoća u kristalu, uprosječena po prostoru i vremenu. Pri određivanju kristalne strukture, ta se elektronska gustoća modelira skupom sferâ elektronske gustoće (koje predstavljaju atome), zajedno s funkcijom 'razmazanosti', tj. parametrima atomskih pomaka kojima se predstavlja gibanje (translacija i libracija) atomâ. Proučavanje ^{2}H i ^{13}C NMR krutinâ pokazuje da ti difrakcijski parametri ne daju potpunu sliku gibanjâ u kristalu. Posebice, parametri röntgenske difrakcije ne daju informacijâ o rijetkim aktiviranim procesima u kristalu niti o gibanjima koja su vezana uz fazne mijene. Dan je niz primjerâ sinergije röntgenske difrakcije i NMR krutinâ: klatnja fenilnih prstenova u solima fenoksipenicilina, rotacija čitavih molekula u halogenidima *ansa*-titanocena, prevrtanje molekule-gosta (cikloheptana, ciklookta-

na) u klatratima tiouree, klatnja i vrtnja kationa u tiourea-piridinijevim halogenidima, zatim kolebanja, vrtnja i fazne mijene u klatratima ferocena i deoksikolne kiseline te, konačno, gibanja, fazne mijene i kiralna selektivnost u klatratima deoksikolne kiseline s *R*- i *S*-kamforom. Posebna je pozornost posvećena pridobivanju informacijâ o mehanizmu faznih mijena iz NMR spektara krutinâ.