Solid State Carbon-13 N.M.R. Studies of Chemical Shift Anisotropy and Ring Rotation in the Plastic Phases of $[(C_6H_6)Fe(C_5H_5)]^+[AsF_6]^-$

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Variable temperature ^{13}C n.m.r. measurements of chemical shift anisotropy in a powdered sample of $U(C_6H_6)Fe(C_5H_5)]^+[AsF'U]^-$ (**1**) reveal phase transitions between three different crystal forms, each characterised by a different combination of internal ring rotations and external rotations of the whole cation.

Compound (**1**) is part of a series of charge transfer catalysts[1] which display an important range of solid state dynamics.[2,3] In (**1**) the cation rotations are thought to involve interactions between neighbouring carbocyclic rings, though no ring motion has ever been observed. The disorder in these compounds has previously been studied by iron-57 Mössbauer spectroscopy and by *X*-ray diffraction.[3] However, these techniques are insensitive to many rotational processes, and to date the only known structure is that of the title compound (Figure 1). Recent advances in high-power cross-polarisation n.m.r. spectroscopy now allow efficient measurement of ^{13}C chemical shift anisotropy (C.S.A.) tensors, and it has been shown[4,5] that such measurements can provide an accurate probe for molecular rotation in plastic solids such as (**1**).

$$[(C_6H_6)Fe(C_5H_5)]^+[AsF_6]^-$$
(**1**)

The experimental ^{13}C C.S.A. patterns of (**1**) are shown in Figure 2 together with the corresponding theoretical spectra calculated from equation 3.7 of ref. 4. Chemical shifts are given with respect to $SiMe_4$. Above about 310 K, the cubic α phase of (**1**) has a ^{13}C C.S.A. profile consisting of two completely symmetric lineshapes each centred at their isotropic frequencies with $Tr\sigma(Bz) = 87$ p.p.m. and $Tr\sigma(Cp) = 77$ p.p.m. (Figure 2; Bz = benzene, Cp = cyclopentadienyl). The symmetry of the spectrum arises from the averaging effect of fast external ('whole-body') isotropic rotation of the cations, though the individual behaviour of the rings is not resolved.

Below about 270 K the crystal transforms to a low-symmetry γ phase with a C.S.A. profile consisting of four[6] axially symmetric patterns which overlap in two pairs to give perpendicular components at $\sigma_\perp$ (Bz) = 129 p.p.m. and $\sigma_\perp$ (Cp) = 101 p.p.m., and parallel components at $\sigma_\parallel$ (Bz) = 28 p.p.m. and $\sigma_\parallel$ (Cp) = 2 p.p.m. (Figure 2). This observation shows that the fast external cation rotations of the high temperature phases are quenched, but the four carbocyclic rings each execute rapid axial rotations.

The C.S.A. profile of the intermediate β phase is more

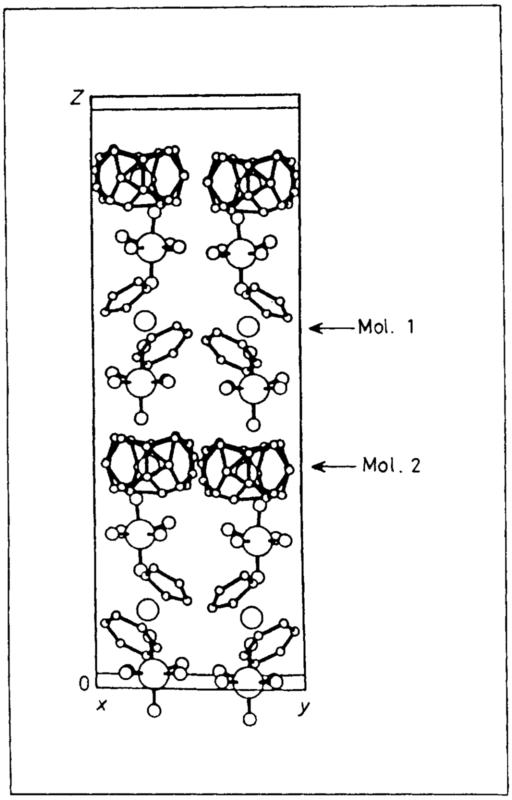

Figure 1. The β phase of (**1**) is monoclinic with eight molecules in the unit cell.[3] The first four molecules are ordered (molecule 1) but the second four molecules are disordered through 90° external reorientations in the xy-plane (molecule 2). X-Ray powder diffraction studies at 330 K show that the structure is cubic at elevated temperatures.

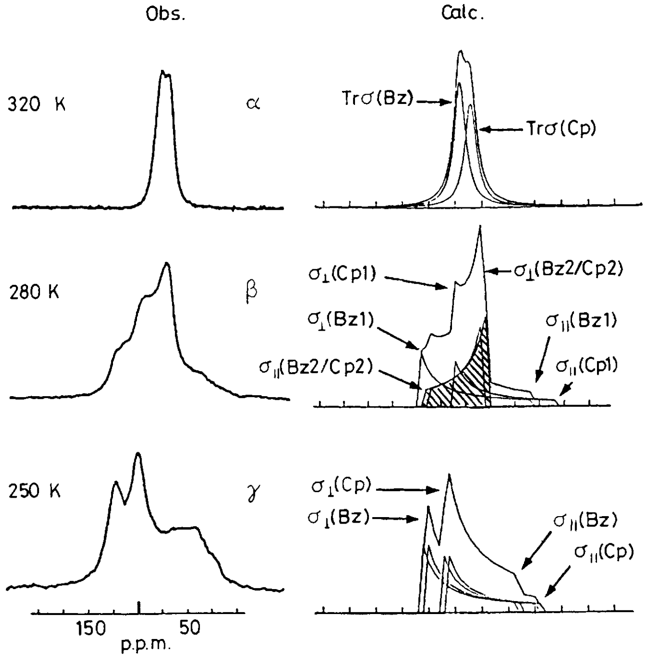

Figure 2. ^{13}C C.S.A. patterns in the solid phases of (**1**). The symmetry of the α phase C.S.A. results from external isotropic rotation of the cations, whilst the axial patterns of the γ phase arise from internal ring rotations. In the β phase ring rotations of molecule 1 lead to axial C.S.A. patterns with components at Bz1/Cp1, whereas molecule 2 exhibits a reversed C.S.A. pattern resulting from the combination of internal and external cation rotations (Bz2/Cp2 shaded). The experimental spectra were recorded using a Bruker MSL-300 spectrometer. The theoretical spectra were calculated from equation 3.7 of ref. 4 with intensity ratio and C.S.A. elements constrained to the experimental values. Chemical shifts are given with respect to liquid $SiMe_4$.

complicated, but the essential features are simulated by a model which combines axial rotation of the carbocyclic rings with xy-plane rotations of the whole cation (Figure 1). Thus, in molecule 1 the disorder is confined to fast internal ring rotations leading to axially averaged C.S.A. patterns having tensor elements which are little different from those of the γ phase with perpendicular components at $\sigma\perp$(Bz1) = 130 p.p.m. and $\sigma_\perp$(Cp1) = 95 p.p.m., and parallel components at $\sigma_\parallel$ (Bz1) = 25 p.p.m. and $\sigma_\parallel$ (Cp1) = 3 p.p.m. (Figure 2).

For molecule 2 the shift tensor elements show a marked change arising from the combination of external rotations of the cation in the xy-plane (Figure 1) together with internal zx-plane rotation of the carbocyclic rings. The effect of the combined motions is equivalent to a rotational exchange between two axial tensors with perpendicular axes. The resulting tensor is still axially symmetric and the trace is unchanged, but the pattern is reversed and its anisotropy is halved[4] to give perpendicular elements at $\sigma_\perp$ (Bz2/Cp2) = 70 p.p.m. and parallel elements at $\sigma_\parallel$ (Bz2/Cp2) = 121 p.p.m. (Figure 2).

The present n.m.r. results show that fast internal ring rotations occur at all lattice sites in both the β and γ phases of (**1**). The γ phase which exists below T_c ~270 K is characterised by quenching of all the external cation rotations but the internal ring rotations persist at least down to 200 K. The cation rotations in (**1**) are important to the crystal structure analysis because the structure of each unit cell is determined not by the static geometry of the molecules but instead by their time-averaged symmetry.

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