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A Broad-line NMR Study on Some Pyrene Complexes: Molecular Motion and Isomorphism in the High-temperature Forms

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Synopsis. The pyrene complexes with six polynitro aromatic compounds are isomorphous to each other above the transition temperatures. The onset of a large degree of molecular motion has been shown from broad-line NMR measurements to occur at the transition temperature of all the six complexes.

As noted earlier,[1] crystalline pyrene complexes with 2,4-dinitrofluorobenzene (DNF), 2,4-dinitrochlorobenzene (DNC), 2,4-dinitrotoluene (DNT), 2,4-dinitrophenol (DNP), and 2,4,6-trinitrochlorobenzene (TNC) exhibit polymorphic transitions. These transitions are of considerable interest because of the isomorphism observed with the high-temperature forms. The disappearance of the specific interaction between the hydrocarbon molecule and the substituent on the acceptor molecule was speculated to be due to dynamical averaging of the interaction by the onset of a large degree of thermal motion at the transition temperature. The presence of such a molecular motion in the high-temperature forms was considered to be consistent with the relatively small enthalpy and entropy changes at the melting of these complexes. Solid state NMR has proven to be powerful tool for the detection and investigation of molecular motion in complexes;[2] therefore, this technique was employed to study the behavior in our cases.

^{1}H NMR spectra were recorded as the first derivatives at 40 MHz, using a JEOL model JES-ME-3X spectrometer with a broad-line NMR attachment, model JES-BE-1, which employs a crossed-coil system. For the measurements, the complexes were pressed in the form of rods with a diameter of 8 mm. Care was taken in recording the spectra to avoid saturation (where possible), and the modulation amplitude was kept small to avoid distortion of line shape. Second moments were calculated for both halves of the derivative curve and corrected for modulation broadening.

Differential scanning calorimetry (DSC) and X-ray diffraction measurements were made as described in a previous paper.[1] In addition to the five complexes mentioned above, the 2,4,6-trinitrotoluene (TNT) complex was found to exhibit a new phase transition at 59 °C, with an enthalpy change of 2.9 kcal mol^{-1}. The complex melts at 162 °C. The enthalpy of melting is 5.3 kcal mol^{-1}. The X-ray diffraction patterns measured using Cu $K\alpha$ radiation are schematically presented in Fig. 1 along with those of the TNC complex for comparison. Although the two acceptor molecules are almost the same in size, the patterns at room temperature are distinctly different, reflecting the nature of the particular substituent. On the other hand, the simple patterns above the transition temperatures are essentially identical and indicate that these high-temperature forms are isomorphous to each other.

The second moment of the measured spectrum is shown in Fig. 2 as a function of the temperature for each of the pyrene complexes. In all the cases, an abrupt reduction in the second moment was observed almost at the transition temperature determined by DSC. Only when the molecules in the high-tempera-

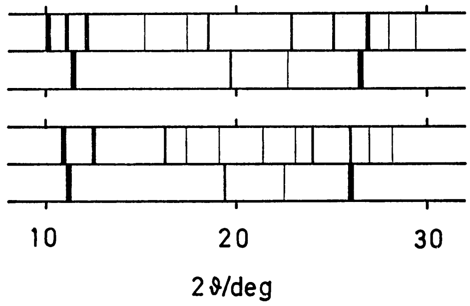

Fig. 1. X-Ray diffraction patterns of the pyrene complexes with a) TNC and b) TNT. The upper pattern for each complex was recorded at room temperature and the lower one, above the transition temperature.

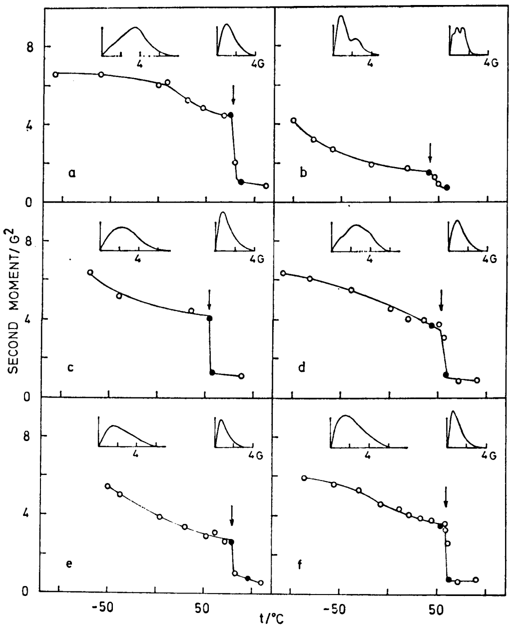

Fig. 2. Second moment values of the proton resonance for the pyrene complexes with a) DNF, b) DNC, c) DNT, d) DNP, e) TNC, and f) TNT with (inset) right halves of representative spectra recorded below (left) and above (right) the transition temperatures. The vertical arrows indicate the thermodynamic transition temperatures.

ture forms are moving fast on an NMR time-scale can one expect such coincidence of the temperatures. It must be noted that the moments observed with the high-temperature forms are in a narrow range around 1 G^2. The resonance line shape changes at the transition. Representative spectra below and above the transition temperature are inset in Fig. 2. The second moments given by these spectra are indicated by shaded circles. Thus, the presence of a large degree of molecular motion in the isomorphous high-temperature forms is now firmly established.

The largest reduction of second moment associated with the transition was found with the DNF complex, and the smallest with the DNC complex. The molecular motion in the low-temperature form of the former complex is clearly more restricted than that of the latter. This conclusion is consistent with the thermodynamic data. Although the enthalpies of melting are rather similar, namely, 5.0 kcal mol^{-1} at 119 °C and 4.2 kcal mol^{-1} at 87 °C respectively, there is a remarkable difference in the enthalpy of transition. The value for the DNF complex is as much as 4.3 kcal mol^{-1}, whereas that for the DNC complex is merely 0.57 kcal mol^{-1}. The enthalpies of transition observed for the other four complexes are in the range from 2.9 to 3.2 kcal mol^{-1}.

The second moment can be calculated from a knowledge of the positions of the nuclei in the lattice, using the formulation of Van Vleck. For such a calculation, the crystal structure is needed, but this is unknown for the present complexes. Nevertheless, the observed variation is so large that the motional characteristics may be discussed to some extent. The second moment in a polycrystalline molecular complex can be divided into an intramolecular part, from the atoms within a single donor molecule and a single acceptor molecule, and an intermolecular part between the atoms of different molecules. For the present complexes, only the former part can be approximately calculated from the molecular structure. The contribution in a pyrene molecule in a rigid lattice has been calculated to be 3.43 G^2 by Fyfe *et al.*3) As for the acceptor molecule, we calculated the intramolecular contribution in DNF, by way of example, to be 1.5 G^2, taking bond distances of C–C=1.39, C–H =1.08, C–F=1.31, and C–N=1.46 Å, and all bond angles 120°. Then, the contribution in the basis unit of the pyrene–DNF complex becomes about 3.2 G^2 for the rigid lattice model. In order to explain the observed second moment in the high-temperature form, a reduction of the moment by some molecular motion has to be taken into consideration.

The rotation of the pyrene molecule in solids has been suggested to occur in pyrene itself and in some of the molecular complexes.3,4) It has been pointed out that the rotational barriers found for complexes are lower than those for the parent compounds, possibly due to a general decrease in intermolecular steric effects;2,5) thus the flat hydrocarbon molecule in the present complexes is probably rotating around the axis perpendicular to the ring plane at high temperatures. Such a motion would reduce the intramolecular contribution by a factor of one fourth.6) Moreover, the intermolecular contribution is also significantly reduced by it. In the case of the DNF complex, the latter contribution appears to be almost nil. As has been suggested for the azulene-trinitrobenzene complex by Fyfe and Kupferschmidt,7) it is likely that the acceptor molecule is also mobile in the high-temperature form. In addition to the pyrene complexes reported here, we have recently found a isomorphous high-temperature forms with the complexes of some other hydrocarbons. The work on these complexes is now in progress and will be the subject of forthcoming papers.

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