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Dynamic Structures of Organic Solids

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Dynamic Structures of Organic Solids

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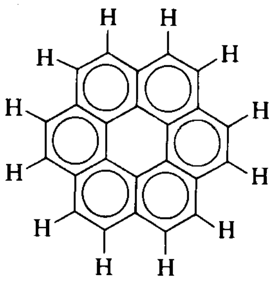
The individual molecules in many solids and solid-like compounds show a high degree of mobility and this may be important in understanding their physical characteristics.[1,2] N.M.R. spectroscopy has proven to be a very versatile technique for the investigation of molecular solids and complements well other techniques such as x-ray crystallography, and dielectric and heat capacity measurements.

Proton n.m.r. spectra of solids are dominated by the direct dipole–dipole interactions between the nuclei which give rise to very broad, featureless absorptions (wide-line n.m.r). In solution these interactions are averaged to zero, giving the high resolution spectra with which most chemists are familiar. The presence of motion in the solid state gives a partial averaging of the dipolar interactions and a narrowing of the n.m.r. absorptions. The relaxation times of the nuclei (T_1, $T_1\rho$) are also sensitive to the presence of molecular motion which provides a relaxation mechanism, a single motion giving a characteristic "V" shaped curve when log T_1 is plotted against $1/T$ from which the activation energy for the motion can be obtained. A combination of these measurements with data from other techniques can give a description of the dynamic structure of the solid.

Thus the ^{1}H n.m.r. linewidth changes in coronene (1) must be due to a movement of the molecule in its molecular plane by 60° jumps[3] ($E_a = 5.9$ kcal m^{-1}), as the x-ray structure shows no evidence for disorder. With less symmetrical molecules, for example acenaphthalene (2) the same type of motion is detected by n.m.r.,[4] but this now introduces disorder which is detected by heat-capacity[5] and x-ray diffraction measurements[6] (the disorder in fact preventing the determination of the room temperature crystal structure).

(1)



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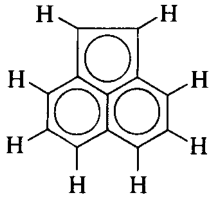


In some cases the motions may be quite complex. For example, in the π-π molecular complex of naphthalene with tetracyanobenzene there is a dynamic disordering of the naphthalene molecules (Figure 2). Wide-line proton n.m.r. and relaxation-time measurements[7,8] (Figure 1) indicate that the naphthalene molecules undergo two complex motions (Figure 2). At low temperatures the molecules jump over the small potential barrier and at

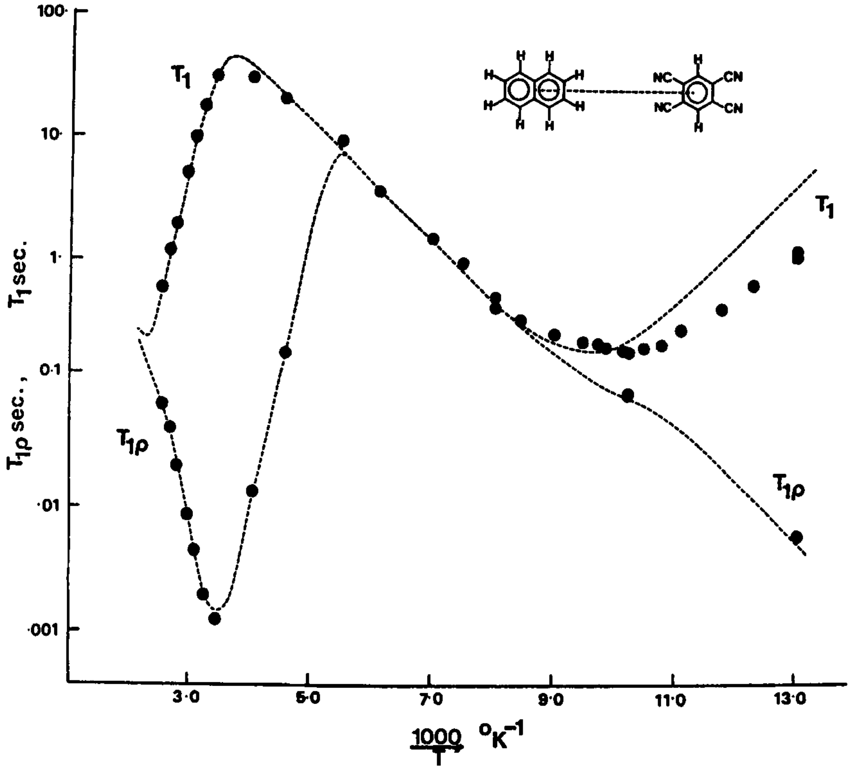


FIGURE 1 Plots of T_1 and $T_{1\rho}$ on a logarithmic scale against the reciprocal of absolute temperature for the proton resonance of the solid naphthalene + TCNB complex. Ref. 8.

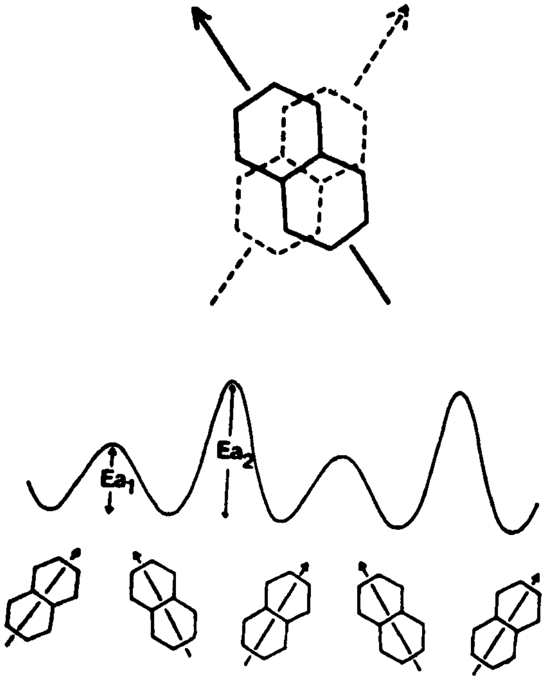
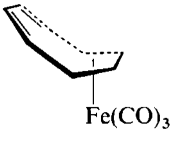


FIGURE 2 Schematic representation of the relationship of the potential energy profile for the motion of the naphthalene molecules in the naphthalene + TCNB complex to the two possible disordered orientations. Ref. 8.

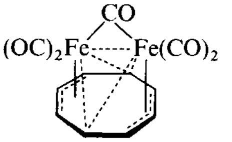
higher temperatures over the larger barrier as well. The T_1, $T_1\rho$ measurements yield barriers of $E_{a_1} = 2$ kcal m^{-1} and $E_{a_2} = 10$ kcal m^{-1} respectively.

Our recent work has shown that even more localized bonding between components need not lead to rigid structures in the solid state. Thus, there is still motion of the organic rings in the fluxional organometallics (**3**)–(**5**)[9–11] (with activation energies 9.1 kcal m^{-1}, 2.6 kcal m^{-1} and 5.2 kcal m^{-1} respectively). Comparison of the n.m.r. data with the x-ray structure of (**3**), which shows localized positions for all the atoms, indicates that only the ring is moving and that it must be by a jumping motion and one where the ring distorts and changes geometry as it moves and the points of localized bonding to the iron are constantly changing. This process is similar to that postulated to occur in solution and can be characterized unambiguously in the solid state. Similar processes occur in (**4**) and (**5**). Even formally localized σ-bonding need not prevent motions in the solid, complexes of type (**6**) also showing motion of the organic moiety.[12]

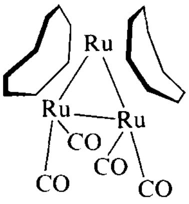
Proton n.m.r. measurements on solids may thus be used to investigate their dynamic structures. They yield little information, however, about the



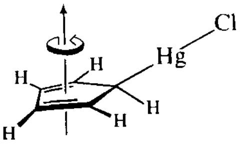
(3)



(4)



(5)



(6)

molecular structures or of the motions of individual parts of molecules (except by inference or by comparison with data from other sources). In recent years pulse-Fourier-Transform techniques have made routine the measurement of ^{13}C spectra in solution.[13] They also make possible the observation of ^{13}C spectra in solids.[14] In the solid state, because of the low natural abundance of ^{13}C (1.1 %) there are no direct carbon–carbon dipolar interactions as exist between protons. The proton–carbon interactions can be removed by powerful proton decoupling fields and the residual broadening due to the carbon chemical shift anisotropy may be averaged by

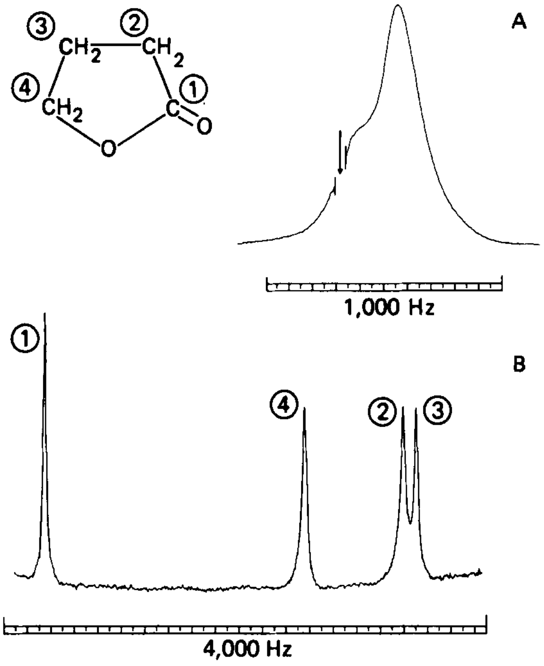


FIGURE 3 NMR spectra of the solid intercalate of butyrolactone in the synthetic sheet silicate Laponite B under normal high-resolution conditions. A. ^{1}H spedtrum (80 MHz). The arrow indicates a sharp peak from HOD in the lock sample. B. ^{13}C spectrum (20 MHz) under the same conditions. Ref. 17.

the "Magic-Angle" spinning at ~3–6 kHz introduced by Andrew,[15] yielding the *isotropic* ^{13}C spectrum.[14] In addition, the S/N can be increased using cross-polarization techniques developed by Waugh and co-workers.[15]

In cases where there is considerable motion of the molecules, the proton spectrum will be relatively narrow and the ^{13}C shift anisotropy averaged out. In these cases, it is possible to obtain spectra using a conventional high-resolution spectrometer. Figure 3 shows the ^{1}H and ^{13}C spectra obtained for the butyrolactone intercalate of the synthetic sheet-silicate Lapoinite-B where the organic molecules are thought to be enclosed between the silicate sheets and illustrates the higher resolution of the ^{13}C spectrum.[17] Spectra of other materials such as liquid crystals[18] and plastic crystals[18,19] may also be easily obtained using a high resolution spectrometer (although in the former case the shift anisotropy is not averaged, the molecules are highly aligned and single carbon values result).

In other cases where little or not motion is present, the ^{13}C shift anisotropy must be removed by spinning at the magic angle. This is illustrated in Figure 4. Several groups have recently implemented these techniques,[20,21] and

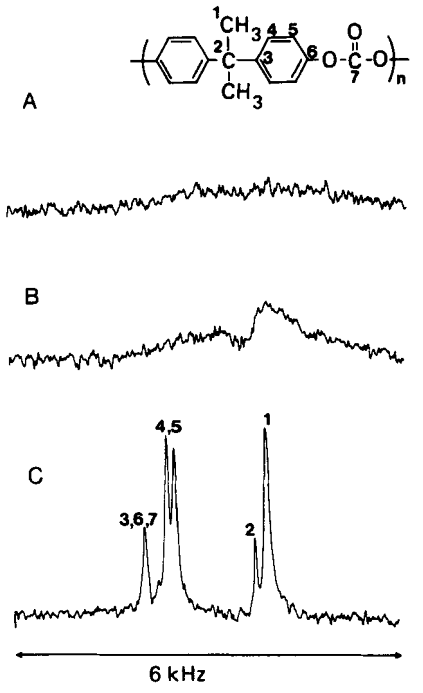


FIGURE 4 ^{13}C spectrum a solid lexan rotor. A. Under normal high-resolution conditions. B. With high-power proton decoupling. C. With high-power proton decoupling and Magic Angle Spinning at 3 kHz.

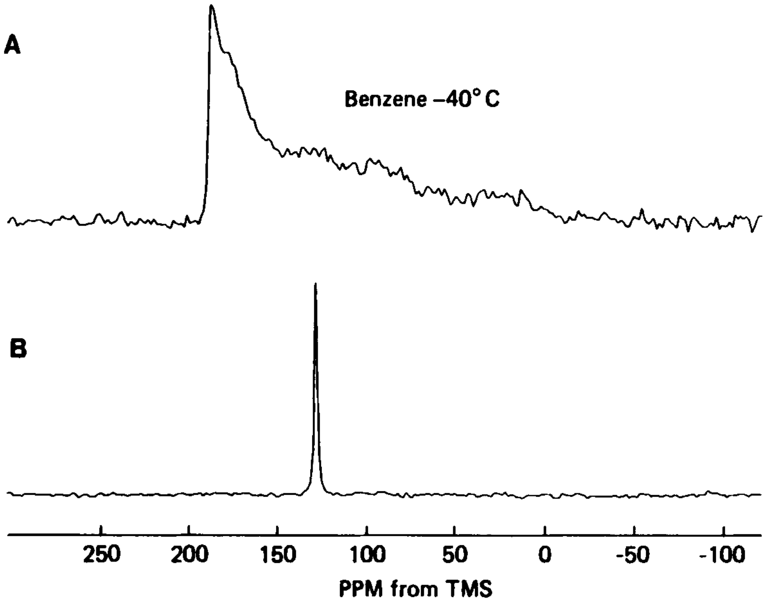


FIGURE 5 ^{13}C spectrum of frozen, solid benzene at −60° obtained using cross-polarizatio techniques. A. Spectrum of a static polycrystalline. B. Polycrystalline sample in a hollo Kel-F rotor spun at the Magic Angle at 3 kHz. Ref. 23.

Schaefer and Stejskal[20] have delineated their application to glassy polymers and explored in some detail the type of information that can be obtained for these systems.

We have designed a simple, efficient spinner device which can be easily and routinely used with a conventional type of probe.[22] The apparatus works well with solid rotors, and with polycrystalline material. It is also capable or working over a large range of temperatures. This is illustrated in Figure 5 which shows the spectrum of solid, frozen polycrystalline benzene,[23] using cross-polarization techniques with and without magic-angle spinning. Figure 6 shows spectra obtained for a crystalline polymer at both −80°C and room temperature.[24] The ability to vary the temperature over a large range is important in order to fully exploit the resolution in the ^{13}C experiment. Thus, it should be possible to obtain information regarding the motions of specific groups in molecules in the solid state from the temperature dependence of the relaxation-times of the individual carbon signals in spectra such as those in Figure 6. Further, there will often be an optimum temperature for the utilization of the cross-polarization technique for signal enhancement.

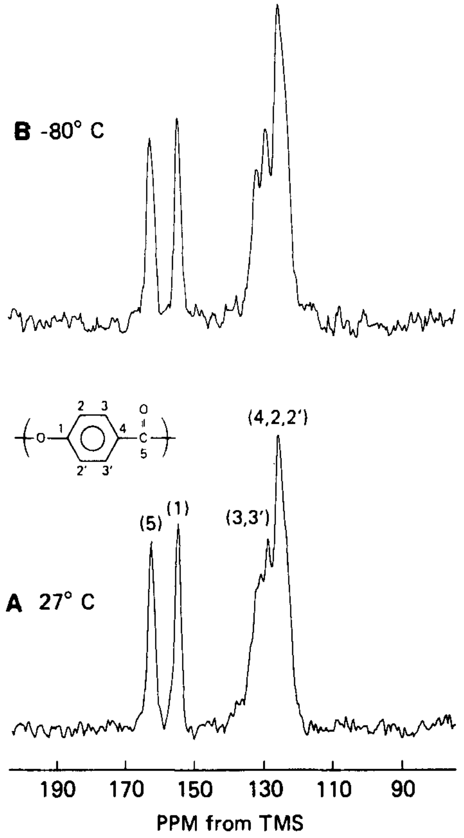


FIGURE 6 ^{13}C N.M.R. spectra obtained using cross-polarization techniques and magic-angle spinning on the crystalline polymer shown. A. At 27°C. B. At −80°C. Ref. 24.

The high-resolution ^{13}C measurements may also be used to investigate chemical exchange processes in the solid state, distinguishing directly between motions which involve a chemical exchange process from simple molecular motions which do not. Thus, since in the ^{13}C spectrum the magic-angle spinning has produced the isotropic values for the chemical shifts, only a chemical exchange process can give further averaging to produce a single absorption for chemically inequivalent carbons (situation analogous to that in solution). This is illustrated in Figure 7 which shows the high resolution ^{13}C spectrum of (**6**) in the solid state.[25] A single sharp signal is observed for all sixteen ring carbons in the complex, detecting directly the fluxional chemical exchange process infered earlier from a comparison of data from ^{1}H n.m.r. measurements with the x-ray crystal structure. We have recently succeeded in obtaining spectra with magic angle spinning techniques at 77 K[25] which

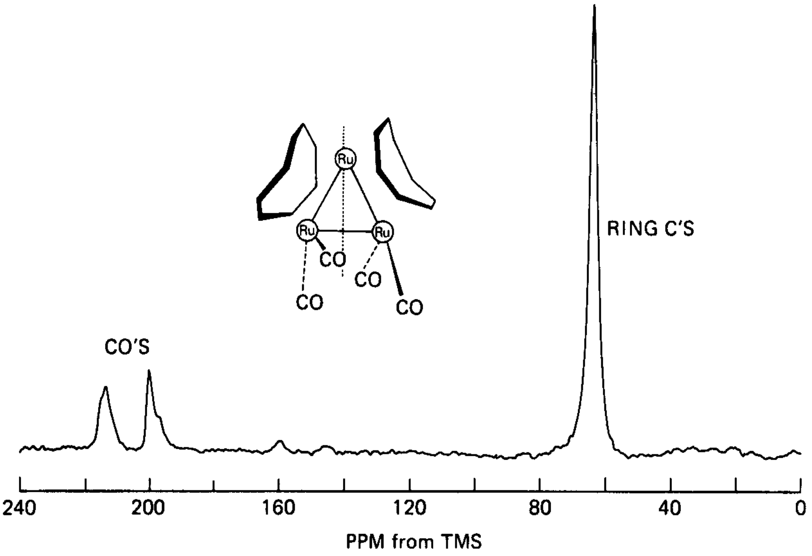


FIGURE 7 A. Schematic representation of the molecular structure of bis(cyclooctatetraene) triruthenium tetracarbonyl in the solid state. B. High resolution ^{13}C spectrum at 30°C run as a polycrystalline sample in a hollow Kel-F rotor with high-power proton decoupling, cross polarization and magic angle spinning. The proton decoupling field was 7 gauss, the cross-polarization contact time 5 msec, the delay time 1 sec and the spinning frequency approximately 3 kHz. 3,000 F.I.D.'s were taken. Ref. 25.

will make possible the investigation of chemical exchange processes of very low energy not observable in solution and also the characterization of reactive intermediates frozen in the solid.

In general, high resolution ^{13}C n.m.r. of solids, combined with ^{1}H n.m.r. measurements may be made on a whole variety of organic materials and in the future will provide detailed information on both the static and dynamic structures of organic solids.

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