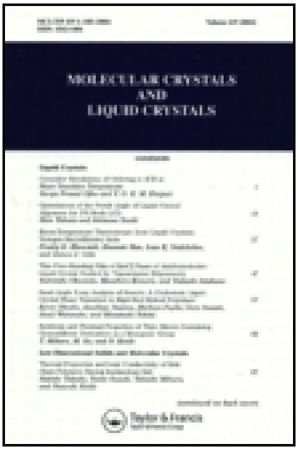

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Phase Transitions in 5,6-dioxycarbonyl[2.2.1]bicyclohept-2-ene

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The temperature dependence of phase structure in 5,6-dioxycarbonyl [2.2.1] bicyclohept-2-ene was investigated by DSC, X-ray diffraction, optical microscopy and ^{1}H NMR. The existence of an endotherm in DSC, loss of optical anisotropy, formation of diffuse diffraction patterns and drastic changes in ^{1}H NMR relaxations indicated the formation of a 'plastic crystal' phase, well below the melting point. NMR relaxation rates were measured as a function of temperature. There are sharp changes in relaxation rates at the plastic crystal transition. The transition introduces rapid molecular rotation, without translation. T_{1H} relaxations show a change in magnitude for the rate, but no change in relaxation mechanism.

INTRODUCTION

Mesomorphic behavior has not previously been reported for 5,6-dioxycarbonyl [2.2.1] bicyclohept-2-ene, Figure 1. Mesomorphic materials do not lose positional, orientational and conformational order abruptly at one temperature during the melting process. These materials go through an intermediate state where one of the three freedoms have at least partly been achieved. Solids which show orientational disorder but positional order below the melting point are called plastic crystals.[1]

Plastic crystals are disordered, liquid like solids usually spherical or globular in shape with a high degree of rotational freedom in the solid state. They are characterized by high vapor pressure, high dielectric constant in comparison with other solids[1] and a large entropy change at the plastic crystal transition with only a small entropy change on melting.[1–3] Due to the substantially liquid like character

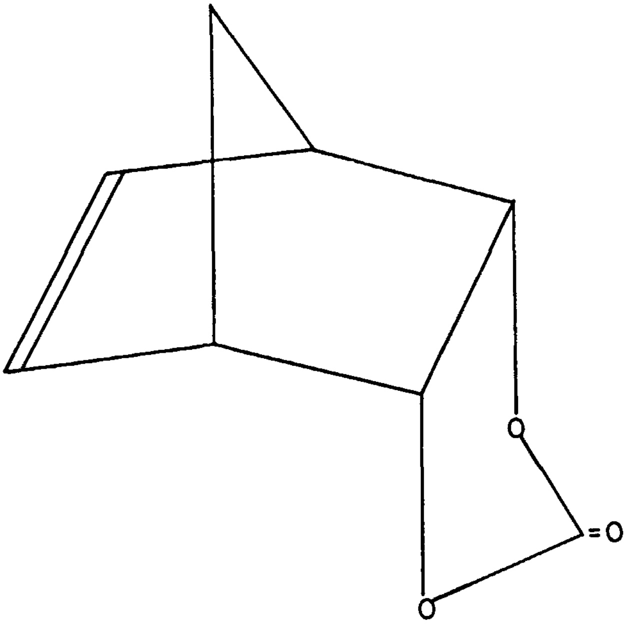

FIGURE 1 5,6-dioxycarbonyl [2.2.1]] bicyclohept-2-ene.

of plastic mesophase X-ray diffraction studies of plastic crystals reveal a relatively small number of reflections with considerable background scattering.[1]

The sensitivity of NMR to molecular motion makes it an ideal tool for analysis of phase transitions in plastic crystals.[4-13] Phenomena such as molecular rotation, libration and diffusion have strong effects on spin lattice (T_1), spin spin (T_2) and spin lattice in the rotating frame ($T_{1\rho}$), relaxation rates for ^1H, ^{13}C and ^2H, as well as quadrupolar splitting for ^{14}N and ^2H in plastic crystals.[4-13] High, MHz (T_1), very low, close to 0 Hz(T_2), and intermediate, KHz($T_{1\rho}$) frequency motions can be well characterized by NMR relaxation rates. Any process which causes fluctuations in magnetic fields at a nucleus will lead to relaxation, and the correlation function which describes molecular motion may be quite complex. However, it is generally possible to analyze the contributions of rotations, librations and diffusion and define the spectral distribution of motions by selection of the proper experiment. The nature of the solid state changes controls the NMR relaxation rates. Abrupt changes in the probability of a transition, and/or frequency distribution of motion is characteristic of the solid/plastic transition.

The onset of a plastic crystal transition occurs with loss of rotational order, without the loss of positional order, so that macroscopic order is lost, but molecular motions are still correlated. In effect, the material is an isotropic solid. NMR relaxation rates reflect these characteristics. Motional narrowing decreases the second moment of the NMR absorption, decreasing line widths by an order of magnitude at the transition giving much larger spin spin(T_2) relaxation times. As temperature is further increased, T_2 continues to increase rapidly until the melting point is reached. T_2 then continues to decrease, but at a much slower rate. T_2 behavior as a function of temperature, therefore, can define the temperature range of plastic crystal behavior.

Spin lattice (T_1) relaxations are quite sensitive to local interactions of plastic crystals and can identify the types of motions responsible for the phase behavior. A minimum T_1 is expected when the temperature is such that the spectral density at the Larmor frequency is a maximum.[14] The slope of the T_1 curve at temperatures above and below the T_1 minimum characterize the spectral density and activation energy for motion at a given temperature. The increased rotation which comprises the plastic crystal transition changes the probability of spin lattice relaxation, giving a discontinuity in a T_1 curve at the transition. The plastic/liquid transition in contrast, may have no such discontinuity implying no drastic change in the probability of molecular reorientation. The energy of activation for molecular reorientation in the various phases determines the dependence of NMR relaxation rates on temperature.

The melting point of 5,6-dioxycarbonyl [2.2.1] bicyclohept-2-ene has been reported as 115°C,[15] but the plastic crystal formation has not been reported previously. We present here results from DSC, polarizing microscopy, X-ray and NMR studies. Thermal analysis demonstrates three endotherms on heating attributed to the crystal/crystal, crystal/plastic crystal and plastic crystal/liquid transitions. Polarizing optical microscopy showed a loss of optical anisotropy, without melting, at 69°C with formation of a liquid phase at 115.2°C. NMR T_2 relaxations show an initial loss of order with decreased line widths at 60–70°C followed by formation of an isotropic liquid at 120°C. T_1 relaxation measurements do show a discontinuity at the solid/plastic transition, but no change in slope, implying a sharp decrease in the probability of relaxation, but no change in the motions responsible for T_1 relaxations. There is no such discontinuity at the melting point, but there is a sharp increase in T_1 10 degrees above the melting point. The results are explained in terms of rapid rotation at the plastic crystal transition, and dissociation to an isotropic melt at higher temperatures.

EXPERIMENTAL

5,6-dioxycarbonyl [2.2.1] bicyclohept-2-ene, was prepared by Diels-Alder reaction between vinylene carbonate and cyclopentadiene.[15] A mixture of 1 gm of hydroquinone, 35 ml toluene, 6 gm Vinylene carbonate and 34.3 gm of dicyclopentadiene was heated to 160°C for 18 hours in a Parr reactor. The reactor was then cooled and reaction product distilled to remove the toluene and excess vinylene carbonate. Distillation of the residue at 137–140°C, $\approx$ 2 Torr, gave the desired product in >99% yield, (m.p. 115.2°C). Three crystallizations with carbon tetrachloride and petroleum ether gave pure 5,6-dioxycarbonyl bicyclo [2.2.1] hept-2-ene.

Optical properties were examined by Olympus BH-2 microscope equipped with Mettler-FP80 hot stage. A photometer coupled to a strip chart recorder was attached to the microscope to measure the depolarized light intensity.

The thermal properties were investigated by means of a Perkin Elmer DSC-2C with a heating rate of 20°C/min.

NMR: The instrument was a General Electric GN-300 with a 300.1MHz frequency for protons. The accuracy of the temperature setting was tested with ethylene glycol.[16] Temperatures were accurate to ± .1°C.

T_{2H} values were measured by a Carr Purcell sequence[17] with delay times between 100μs and 100ms. A cycle time of $5 * T_1$ was used in each case, with 60 coadded spectra.

T_{1H} were measured with an inversion recovery sequence,[18] using delay times between 40μs and 20s. 60 scans were coadded to improve the signal to noise ratio.

The crystalline sample was poured into a 5mm NMR tube which was then heated to 145°C for 30 minutes to melt it and provide a homogeneous sample. The sample was slowly cooled to 0°C and maintained there for 1 hour to ensure complete crystallization. Solution state spectra of the sample before and after treatment showed no changes. The results obtained without this treatment were essentially the same, but the sample inhomogeneity significantly increased line widths at the solid/plastic transition. Repeat runs on the same and different samples showed the identical results.

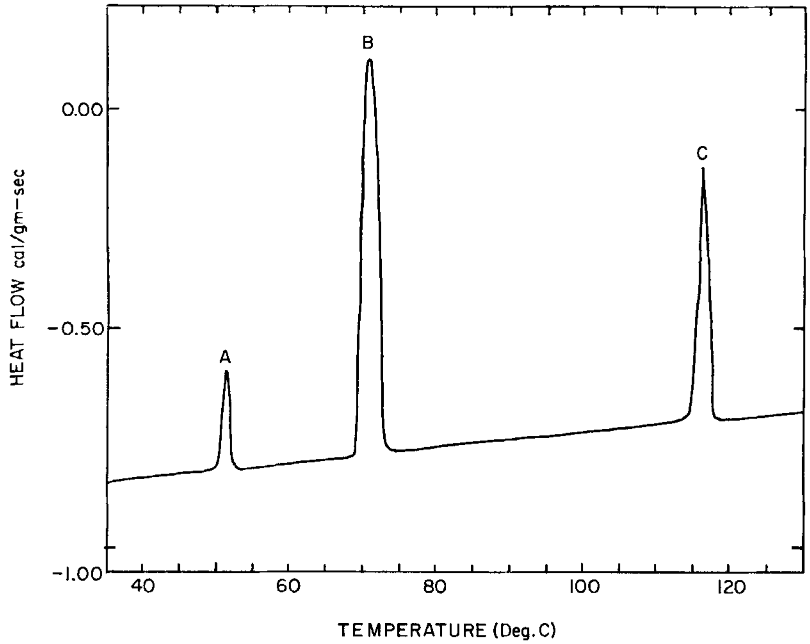

FIGURE 2 DSC thermogram of 5,6-dioxycarbonyl [2.2.1] bicyclohept-2-ene, showing the endotherms for A) crystal/crystal; B) crystal/plastic crystal and C) plastic crystal/melt transitions.

RESULTS AND DISCUSSION

Reported m.p. for 5,6-dioxycarbonyl [2.2.1] bicyclohept-2-ene is 115°C.[15] A DSC scan, Figure 2, showed endotherms at 50.4, 69.2, and 115.2°C. Temperatures of these transitions did not vary on repeated heatings in the DSC. On cooling to 30°C, two exotherms were observed at 39.1 and 113.5°C, related to last two transitions in the heating cycle. The low temperature transition is supercooled to below 30°C on cooling. Supercooling for the high temperature endotherm is comparatively much smaller (1.8°C) than the low temperature endotherms. The enthalpy and entropy of transition are listed in Table I. The entropy of transition for the endotherm at 69.2°C is much higher than the entropy change involving the other two transitions.

Polarizing microscopy showed that the crystals of this compound, which are bright and birefringent at room temperature, become optically isotropic without fusing or change of shape at 69°C. The crystals melted at 115.2°C giving a viscous fluid, like the melt of any crystalline organic material. Thermal transitions were also followed by light

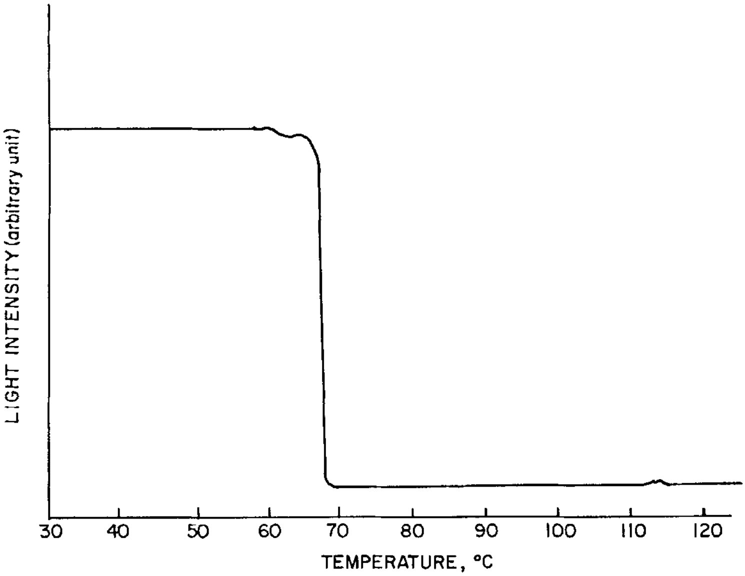

FIGURE 3 Depolarized light intensity as a function of temperature for 5,6-dioxycarbonyl [2.2.1] bicyclohept-2-ene.

intensetometer, Figure 3. No change in polarized light intensity occurs below 69°C where intensity dramatically decreases to nearly zero corresponding to loss of optical anisotropy. There is very little change at the melting point, 115.2°C. The endotherm at 69.2°C is the crystal to plastic crystal transition. A first order transition before this, at 50.4°C, without any detectable change in polarizing microscopy is attributed to a crystal/crystal transition. This is not surprising, since materials which form plastic crystals are often polymorphic solids.

Calorimetric and polarizing microscopic observations, especially the loss of optical anisotropy before complete melting are unusual

TABLE I

Enthalpy and entropy of phase transitions for 5,6-dioxycarbonyl [2.2.1] bicyclohept-2-ene

Temp. °C	ΔH J(mol)$^{-1}$K^{-1}	ΔS J(mol)$^{-1}$K^{-1}	Supercooling °C
50.4	0.9	2.9	—
69.2	8.7	25.5	30.1
115.2	3.6	9.3	1.8

for crystalline organic solid. A considerable gain in entropy before complete melting, with the loss of optical anisotropy and only a small entropy change at the melting point, is characteristic of "plastic crystal" phase between these two temperatures. Above 69°C the molecules have rotational freedom. Translational freedom is then gained on melting at 115.2°C. Since the melting transition in plastic crystals involves only positional disordering, the entropy gain is small in comparison with melting of normal organic crystals. ΔS for the plastic crystal to isotropic fluid transition is independent of molecular size, usually between 7 and 14 $J(mol)^{-1}K^{-1}$. The entropy change for melting at 115.2°C is 9.3 $J(mol)^{-1}K^{-1}$, Table I, which is well within the expected range.

Plastic crystalline behavior was confirmed by X-ray diffraction and NMR spectroscopy. X-ray powder diffraction were obtained at room temperature and at 75°C. Sharp rings observed at room temperature, became diffuse at 75°C due to loss of rotational order in the plastic crystal.

^1H NMR spectra for the solid, plastic and liquid phases are presented in Figure 4. In a solid sample, which retains its shape, the sharp line width decreases are good evidence of plastic crystalline behavior because rotational freedom in this state is what narrows the lines. Line width which decreases abruptly above 60°C (333K), continues to fall rapidly until the melting point is reached. This is very similar to other plastic crystals.[1,4,5]

The change in $1/T_{2H}$ as a function of $1/T$, Figure 5, is consistent with plastic crystal behavior. The decreased line width observed between 220K and 333K can be attributed to the onset of rotational motion in the solid phase below the plastic crystal transition. Motional narrowing becomes more pronounced between 338K and 388.2K (115.2°C) giving progressively sharper lines, but complete narrowing is not observed until the temperature exceeds the melting point by 10 degrees. The slope of the curve changes above the melting point, because the relaxation mechanism changes as translational freedom increases. At the melting point, the observed line widths are still relatively large for liquids, but the sample temperature is quite close to the melting point and the viscosity is high. Further decreases in line widths are observed at still higher temperatures, as one might expect. After melting the response is as expected for a high resolution NMR spectrum, with line widths decreasing smoothly as a function of temperature.

The spin lattice relaxation time, T_{1H}, also changes as a function of temperature, Figure 6. The T_1 minimum is observed close to 30°C.

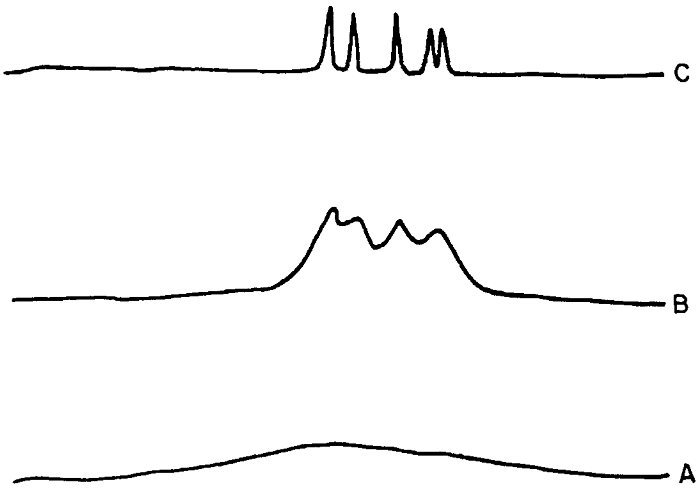

FIGURE 4 ^{1}H NMR spectra of 5,6-dioxycarbonyl [2.2.1] bicyclohept-2-ene in the A) crystal; B) plastic crystal and C) liquid phases.

A discontinuity in the T_1 vs temperature curve is observed at the plastic crystal transition. There is no such discontinuity at the melting point, 115.2°C. Above the melting point, T_{1H} increases rapidly, as one would expect for a free flowing liquid.

Despite the discontinuity at the solid/plastic transition there is no change in the slope. Therefore the relaxation mechanism must remain essentially constant throughout the 30°C–125°C range. It is quite surprising that the major relaxation mechanism in the plastic phase, is also the dominant relaxation pathway in the solid phase and liquid phase close to the melting point. The rapid increase in T_{1H} above 125°C is due to a change in relaxation mechanism from molecular rotation to translation. The molecular motion close to the melting point must have the same frequency distribution suggesting no difference in motion just below and just above the melting point. Presumably, the molecules are still somewhat associated in the viscous liquid obtained at the melting point. As the temperature increases the motions are no longer correlated, individual molecular collisions control spin lattice relaxations and the slope of the T_1 curve changes.

The interpretation of these NMR relaxation phenomena is not straightforward, but certain points are clear. T_1 and T_2 relaxation behavior confirms the formation of a plastic crystal phase between 69°C and 115.2°C. The transition from solid to plastic phases causes a sharper discontinuity for T_1 than T_2. T_{2H} is sensitive to small changes

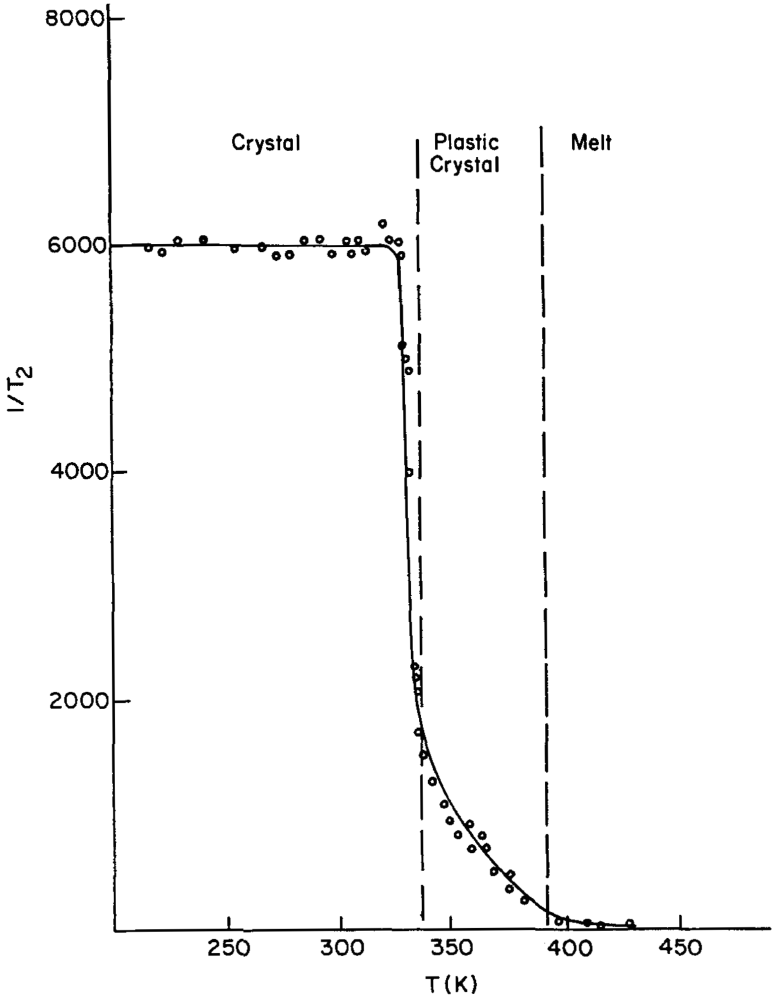

FIGURE 5 Temperature dependence of $1/T_{2H}$.

in long range order, while T_1 will reflect local phenomena. The solid/plastic crystal transition is sharper in the T_1 case because the loss of long range order below the plastic crystal transition is not severe enough to significantly change the local molecular environment. The T_2 measurements show a slow decrease in order below the temperatures expected from DSC measurements, and optical microscopy because the extent of molecular rotation in the solid phase increases with temperature. The increased rotation reduces the long range

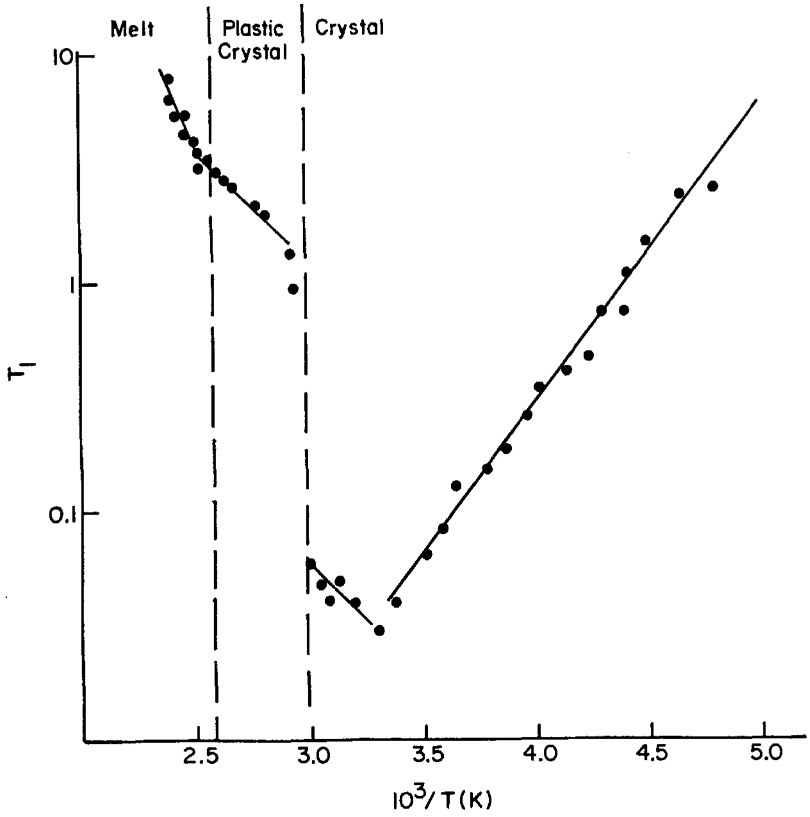

FIGURE 6 Temperature dependence of T_{1H}.

correlation of the system, but not enough to seriously affect macroscopic orientation below the solid/plastic transition, where the higher probability of molecular rotation causes enough macroscopic disorder to be observed by bulk measurements such as DSC and polarizing microscopy.

The step change in the magnitude of T_{1H} at the solid/plastic transition signifies a substantial increase in the total molecular mobility of the system, but the constant slope on both sides of the transition means the motion responsible for relaxation at the Larmor frequency has not changed. Increased molecular rotation reduces homonuclear dipolar coupling. However, the frequency of rotation is probably too high to provide efficient spin lattice relaxation. The plastic crystal transition provides new modes of motion, and changes the spectral density of motion, but the major change is at too high a frequency to provide T_1 relaxation. The molecules then must relax as essentially isolated spin systems, but the mechanism is the same as in the solid state. Thus, spin lattice relaxation is significantly slower in the plastic phase.

CONCLUSION

The loss of polarization observed by microscopy, the endotherms observed by DSC, and NMR relaxation measurements all show decreased macroscopic order without a loss of local order, i.e. a plastic crystal phase, which persists until the melting point when transitional motion, and formation of an isotropic liquid phase occurs.

5,6-dioxycarbonyl [2.2.1] bicyclophept-2-ene enters a "plastic crystal" state at 69.2°C and melts at 115.2°C, the previously reported melting point.[15]

There is a step change in the amount of molecular rotation at the solid to plastic transition as measured by NMR, but no change in the major spin lattice relaxation mechanism. The plastic phase melts at 115.2°C, with sufficient correlation of the molecules in the viscous liquid that there is again no significant change in relaxation mechanism. When the temperature is increased further, molecular translations and collisions become the dominant types of molecular motion.

Future work on this material will include other types of NMR analysis to better characterize the molecular motions. Measurements of ^{13}C T_1, T_2 and $T_{1\rho}$ as well as solid state ^{13}C NMR techniques such as cross-polarization provide much higher resolution of individual species and the ability to measure relaxation rates at individual sites, for more refined probes of phase dimensions and behavior around the thermal transitions.

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