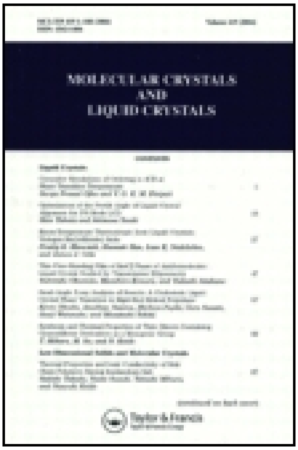

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Molecular Motions in the Solid Rotator Phase of 2-Adamantone: A Thermally Stimulated Currents Study

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Molecular Motions in the Solid Rotator Phase of 2-Adamantone: A Thermally Stimulated Currents Study

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A Thermally Stimulated Discharge Currents (t.s.d.c.) study of 2-adamantanone has been performed in the temperature range from −160 °C to +100 °C in order to analyse the phase transitions and the molecular motions present in this solid. A relaxation was observed at −130°C which was attributed to the transition between an ordered brittle phase and a biphasic system composed by this ordered phase and an orientationaly disordered phase. An higher temperature relaxation was also observed which probably corresponds to the onset of the molecular self-diffusion in the solid. It was suggested that the t.s.d.c. technique is potentially a powerfull technique to study molecular motions in solid rotator phases:

Keywords: Molecular crystals, plastic crystals, reorientational motion, solid-solid transition, order-disorder transition, dielectric relaxation, TSC, TSDC.

INTRODUCTION

Brittle crystals have ordered translational and rotational degrees of freedom. At the opposite, isotropic liquids show both translational and rotational disorder. On the other hand, mesophases exhibit partial degrees of order. Liquid crystals are an example of mesophase where there is long range orientational correlation between the molecules but no long-range positional order. Solid rotator phases are also mesophases but now orientational disorder is present as well as positional order. Crystals composed of highly symmetrical molecules often exhibit solid rotator phases(1–4).

Orientational freedom in a solid does not necessary mean completely free rotation about an axis of the molecule. The mechanism of molecular reorientation in a solid is such that each molecule has two or more equilibrium orientational positions (orientational sites) which are seperated by potential barriers so that the thermal energy can lead the molecules to jump discontinuously from one site to another(3,4).

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If a solid rotator phase is heated up, translational disorder (self-diffusion) may also appear at temperatures below the melting point(4–6). Moreover, a given substance can exhibit different solid rotator phases.

Several experimental techniques have been used in order to study molecular motions and phase transitions in molecular solids showing solid rotator phases, namely Nuclear Magnetic Resonance (n.m.r.), Dielectric Relaxation Spectroscopy (d.r.s.) and Incoherent Quasi-elastic Neutron Scattering (i.q.n.s.). Another technique which proved to be very powerfull to study molecular motions in solid materials is that of Thermally Stimulated Discharge Currents (t.s.d.c.)(7,8). Nevertheless, this technique has not been used until now to study molecular rotations in solid rotator phases(9). This is even more surprising since the t.s.d.c. technique is believed to have a high resolution power arising from its low equivalent frequency(10).

In the present work we report a study, by the t.s.d.c. technique, of the molecular motions in solid 2-adamantanone (2-one-tricyclo[3,3,1,1]decane) which is a globular molecule of symmetry C_{2v}. Calorimetric studies(11,12) showed that this compound exhibits a first-order solid-solid phase transition at $T_t = -95$ °C. On the other hand, a study by single-crystal X-ray diffraction(13) showed that between T_t and the melting point ($T_m = 256$ °C) the solid has a face-centered cubic plastic phase with the dipolar axis (C=O) lying along this six fourfold axis of the cubic lattice. The C=O bond being oriented along a particular [001] axis, the molecule may take only two distinct equilibrium positions corresponding to a $\pi/2$ rotation around the dipole moment axis. The molecular motions in solid 2-adamantanone have been studied before by n.m.r.(14,15), by d.r.s.(16) and by i.q.n.s.(17). In the following we will report our t.s.d.c. results and we will compare them with those obtained by the other techniques.

EXPERIMENTAL

2-Adamantanone was from Aldrich (catalogue *n*° 14,604–8) with a melting point $T_m = 256–258$ °C, and it was used without further purification. The sample was used as a compressed disc of ~0.8 mm thickness which was shaped under the pressure of ~75 Mkg m^{-2}. It was shown(18) (for a sample of a different molecular solid: pentachloronitrobenzene) that the influence of pressure (or density of the disc) on the dielectric relaxation behaviour was such that the strength of the relaxation increased with increasing density, but that its basic features such as the frequency location, the activation energy and the spread of relaxation times were not affected by the densiy of the disc.

Thermally Stimulated Depolarisation Current (t.s.d.c.) experiments were carried out with a TSC/RMA spectrometer (Solomat Instruments, Stamford, CT, USA) covering the range −170 to +400 °C. The parallel electrode assembly has an effective area of ≈ 38 mm^2. A Faraday cage shields the sample, and prior to the experiments the sample, located between parallel plate electrodes, is evacuated to 10^{-4} mbar and flushed several times with 1,1 bar of high-purity helium. In order to analyse specific regions of the t.s.d.c. spectrum, different methods of polarising the sample were used, namely, the so-called t.s.d.c. global experiment and the thermal sampling (or cleaning, or windowing) experiment(19). In both types of experiment the sample was polarised in a given temperature range (with the field applied between T_p and T'_p) the polarisation was frozen in by cooling down to T_0 and the depolarisation current was then measured as the polarised sample was heated up to $T_f > T_p$ at a constant rate. The difference between both types of experiment is that in a t.s.d.c. global experiment $T'_p = T_0$, whereas in a thermal cleaning (TC) experiment $T_p - T'_p = \Delta T$ (the window of polarisation) has a small and constant value (typically 3 °C) and $T_0 \ll T_p$ and T'_p. The technique of *TC* allows thus the polarisation of specific segments of a complex global relaxation . If we assume that the peaks obtained from that method can be characterised by Debye behaviour, we have:

$$\frac{dP}{dt} = -\frac{P}{\tau} \tag{1}$$

where P is the remaining polarisation and τ the relaxation time. The depolarisation current ($I = -dP/dt$) measured as a function of temperature is used to calculate the reaxation time at given temperature[20]:

$$\ln(\tau(T)) = \ln\int_t^{\infty} I(t)dt - \ln(I(T)) \tag{2}$$

The representations of log τ vs $1/T$, the so-called Bucci plots, are useful for the determination of the kinetic parameters associated with the different relaxation mechanisms.

RESULTS AND DISCUSSION

The t.s.d.c. spectrum of 2-adamantanone shows two well separated relaxations (see Fig. 1), one of which is sharp and whose maximum intensity occurs at ~ −130 °C and the other which is broader and begins at ~ −20 °C. The higher temperature side of the t.s.d.c. spectrum was difficult to study due to the tendency of 2-adamantane to sublimate (to evaporate directly from the solid) at temperatures higher than 80–100 °C.

In Figure 1 it can also be observed a discharge near −50 °C whose shape is not characteristic of a thermally stimulated dipolar relaxation process. In fact, it was observed that a spontaneous discharge was present at this temperature in the t.s.d.c. spectrum of the depolarised sample (baseline) and that this spontaneous discharge was enhanced when the sample was polarised*. The relaxation observed at −130 °C

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*It can also be observed from Figure 1 that this discharge is present even when the t.s.d.c. global experiment is carried out in conditions such that the polarising field is applied in a temperature range far below the temperature at which the discharge appears (experiment in Figure 1 where the field was applied between −100°C and −160°C, far below −50°C). On the contrary, in order to activate a dipolar relaxation process it is necessary to apply the polarising field in the temperature region where the peak appears.

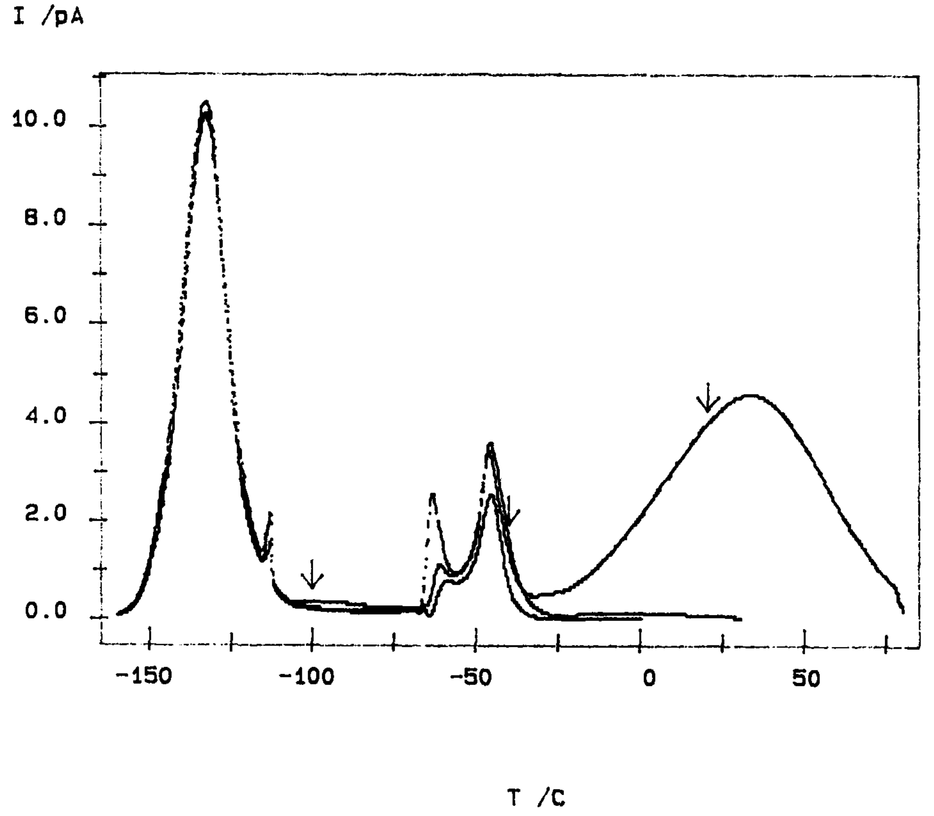

FIGURE 1 The t.s.d.c. global spectrum of 2-adamantanone. The polarisation temperature, T_p, of the three experiments (indicated by the arrow) were −100 °C, −40 °C and 20 °C. The other experimental conditions were: freezing temperature, $T_0 = -160$ °C; heating rate, $r = 8$ °C; electric field strength, $E = 400$ V/mm.

in the t.s.d.c. spectrum of 2-adamantanone (Fig. 1) probably corresponds to the transition between an ordered brittle phase and an orientationally disordered plastic phase which was observed by calorimetry(11,12) and by n.m.r.(14,15) and was reported to occur at −95 °C. It is to be noted the lag between the temperature of −130 °C at which the relaxation appears in the t.s.d.c. spectrum and the temperature of −95 °C obtained from n.m.r. and calorimetric studies. It is interesting to point out in this context that the n.m.r. studies(14,15) showed that the two phases coexist at the same temperature in the temperature range between −95 °C and −125 °C which suggests that the peak obtained in t.s.d.c. corresponds to the transition between the ordered phase and the biphasic region. It is also to be noted that this transition in 2-adamantanone showed an histerisis in both temperature(12) and pressure(21) which is very strong when compared with that observed in other adamantane derivatives. On the other hand, it was observed(12) that the differential scanning calorimetry behaviour of 2-adamantone was strongly dependent on the previous thermal history of the sample so that a limiting behaviour was obtained only after the same sample was subjected to a series of heating-cooling cycles. Oppositely, in our t.s.d.c. experiments the behaviour of the peak at −130 °C did not show any modification from experiment to experiment and from sample to sample.

The global relaxation at −130 °C shown in Figure 1 was decomposed into its components by the thermal cleaning (TC) technique. Figure 2 shows the results of several TC experiments performed in the temperature region where this relaxation appears. These results were analysed by the Bucci method(20) in order to obtain the thermokinetic parameters associated with the different components of this relaxation (the obtained results are shown in Tab. I

It can be seen from Table I that the activation parameters of the TC components of the global relaxation slightly increase as the temperature increases (lower temperature components) and tend to constant values of $\Delta H^{\neq} \approx 12.5$ kcal mol^{-1} and $\Delta S^{\neq} \approx 22$ cal K^{-1} mol^{-1}. We are thus in the presence of a slightly distributed relaxation, conclusion which agrees with the d.r.s. study(16) which showed that this motion has a Cole-Cole distribution parameter near the unity.

Adamantane derivatives in solid rotator phases can undergo two kinds of motion. The first is a uniaxial rotation around the dipole axis, which is of order four in the case 2-adamantanone. This motion is not dielectrically active since it does not lead to a reorientation of the dipole moment. The second type of motion is a tumbling

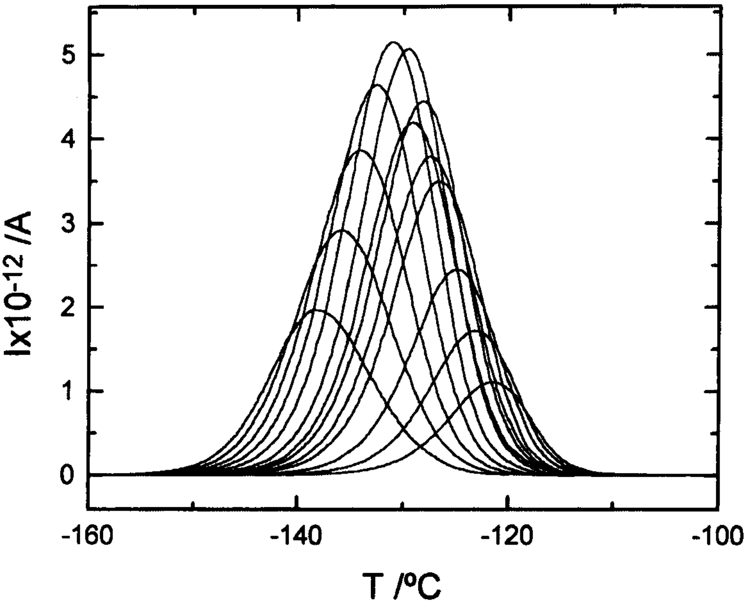

FIGURE 2 Thermally cleaned components of the relaxation at −130°C. The polarisation temperature of the different experiments were: −148, −146, −144, −142, −140, −138, −137, −136, −135, −134, −132, −130 and −128°C. The other experimental conditions were: quenching temperature, $T_0 = -160$ °C; window width, $\Delta T = 3$ °C; heating rate, $r = 8$ °C/min; electric field stregth, $E = 400$ V/mm.

TABLE 1

Activation enthalpy, $\Delta H^{\neq}$, and activation entropy, $\Delta S^{\neq}$, of the *different thermally cleaned components of the relaxation at* -130°C. T_p and T_m are respectively the polarisation temperature and the temperature of maximum intensity of each TC peak.

T_p/°C	T_m/°C	$\Delta H^{\neq}$/kcal mol^{-1}	$\Delta S^{\neq}$/cal K^{-1} mol^{-1}
−148	−138.4	10.7	16
−146	−135.9	10.9	17
−144	−134.2	11.6	20
−142	−132.7	12.2	24
−140	−131.1	12.2	23
−138	−129.6	12.7	26
−137	−129.2	12.4	22
−136	−128.2	12.5	23
−135	−127.5	12.6	23
−134	−126.7	12.5	22
−132	−124.8	12.4	20
−130	−123.2	12.9	23
−128	−121.5	13.2	24

reorientation of the dipolar axis which for 2-adamantanone occurs between the six [001] cubic lattice directions. This motion is dielectrically active and we believe that it is at the origin of the t.s.d.c. peak at −130 °C. This tumbling motion was studied before by different techniques(14−17). Nevertheless, the values of the activation energy reported in the literature are much lower than that of 12.5 kcal mol^{-1} we obtained by t.s.d.c.. In fact, the reported values are 5.0 kcal mol^{-1} (by i.q.n.s(17)), and 3.5 kcal mol^{-1} (by n.m.r.(15) and d.r.s.(16)). This difference between the value of the activation energy obtained by t.s.d.c. and by the other techniques is surprising and will be a subject for future analysis and discussion. As we reported before, the t.s.d.c. studies of molecular motions in solid rotator phases are practically inexistent. Nevertheless, in very recent studies which are under way in our laboratory on hexasubstituted benzenes(22,23) and on cyanoadamantane(24) we obtained values of the activation energy for the motions in the plastic phases which are in very reasonable agreement with those obtained by other techniques. This is the case for pentachloronitrobenzene where we obtained(22) the value of 16 kcal mol^{-1} whereas the value obtained by dielectric relaxation spectroscopy is exactly the same(18,25). For tetrachloro-*m*-xylene our t.s.d.c. value(23) is 12 kcal mol^{-1} whereas the value we obtained by d.r.s. is 10 kcal mol^{-1}(23). For cyanodamantane, on the other hand, our t.s.d.c. value(24) is ~ 16 kcal mol^{-1} whereas values of 12–13 kcal mol^{-1} are reported in the literature(26,27). It is thus clear that in these cases there is no discrepancy between the value of the activation energy obtained by t.s.d.c. and the values obtained by other techniques. Moreover, these activation energy values are of the same order of magnitude as that we obtain for 2-adamantanone by t.s.d.c. (12.5 kcal mol^{-1}), but they are very large when compared with the value of 3.5 kcal mol^{-1} reported in the literature(15,16).

The extrapolation of the Arrhenius lines obtained from the d.r.s and the t.s.d.c. techniques respectively to the frequencies of the t.s.d.c. and d.r.s. experiments can give us some information about this problem. The equivalent frequency of a t.s.d.c. experiment can be calculated by(10)

$$f=\frac{E_a\cdot r}{2\pi\cdot R\cdot T_m^2} \tag{3}$$

where E_a is the activation energy, r the heating rate, R the ideal gas constant and T_m the temperature of maximum intensity of the t.s.d.c. peak. For the *TC* component of the relaxation at -130 °C obtained with a polarisation temperature $T_p = -138$ °C and with a heating rate $r=8$°C/min, the activation energy is 13 kcal mol^{-1} and the location in the temperature axis is $T_m = -129.6$ °C. The equivalent frequency calculated from equation (3) is $f=6.8\times10^{-3}$ Hz. On the other hand, the Arrhenius plot obtained from the d.r.s. studies of 2-adamantanone is described by the equation(16)

$$f_c = 1.252\times10^{12}\exp\left(\frac{1764}{T}\right) \tag{4}$$

where f_c is the frequency of maximum loss of the d.r.s. peaks. If we extrapolate now this equation down to the frequency 6.8×10^{-3} Hz of the t.s.d.c. peak, we conclude that this relaxation which is observed by d.r.s. between -95 °C and 30 °C in the frequency range from 10^8 up to 8×10^9 Hz, should appear at ~ -220 °C in t.s.d.c., a temperature which is far below the temperature range of our experiments. This conclusion suggests that the relaxation studied by d.r.s. in ref.(16) is not entirely equivalent to that we observed at -130 °C by t.s.d.c. On the other hand, if we consider the Arrhenius line of the TC peak obtained with $T_p = -138$ °C, with equivalent frequency 6.8×10^{-3} Hz (and whose Arrhenius parameters are $\log_{10}\tau_0 = -18.55$ and $E_a = 13$ kcal mol^{-1}), and if we extrapolate it up to a frequency of 10^9 Hz (in the frequency range of the d.r.s. experiments), we conclude that this relaxation would have a temperature of maximum loss at ~ 50 °C which is a temperature above the temperature range of the d.r.s. experiments. Even if these extrapolations may be considered as very rough estimations, they nevertheless suggest that the relaxation which appears at -130 °C in the t.s.d.c. spectrum do not correspond exactly to that which was studied by d.r.s. in ref.(16). More research work is obviously needed in order to clarify this problem and to understand the significance of the relaxations observed by the two related dielectric techniques. Nevertheless, from our previous comments we can suggest that: 1) the t.s.d.c. peak occurs at -130 °C (and not at -95 °C) due to the existence of a biphasic region which extends down to ~ -125 °C as was shown by n.m.r.(14); 2) the activation energy of the t.s.d.c. relaxation, which occurs at the onset of the biphasic region, appears to be significantly higher than that observed by d.r.s. and n.m.r., probably as a result of an increase of the activation energy with decreasing temperature along the biphasic region. These suggestions seem to be reasonable if we consider that no thermodynamic transition was observed by differential scanning calorimetry from

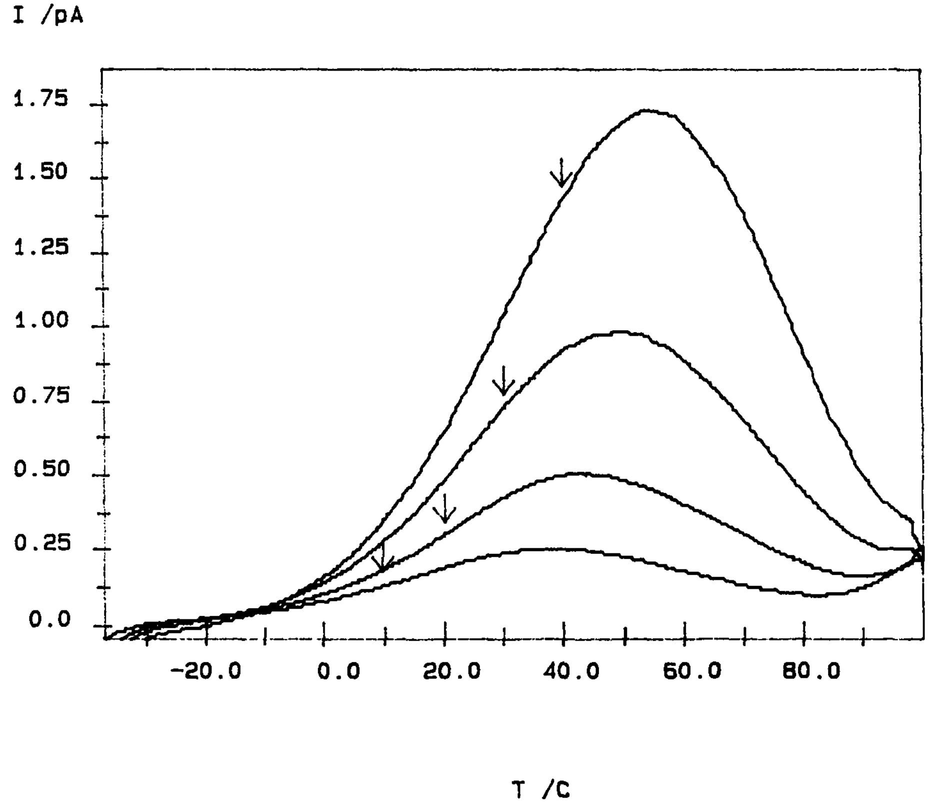

FIGURE 3 Thermally cleaned components of the higher temperature relaxation of 2-adamantanone. The polarisation temperatures were 10, 20, 30 and 40 °C. The other experimental conditions were: quenching temperature, $T_0 = -100$ °C; window width, $\Delta T = 3$ °C; heating rate, $r = 8$ °C/min; electric field strength, $E = 400$ V/mm.

-95 °C down to -150 °C[12] and that the n.m.r. studies[15] seem to show that the molecular motions are frozen in the lower temperature phase.

As shown in Figure 1, another relaxation peak is observed in the t.s.d.c. spectrum of 2-adamantanone, well below the melting point. As emphasized before, this relaxation was difficult to analyse due to the tendency of the sample to sublimate. Figure 3 shows the results os some TC experiments obtained in the temperature where this relaxation appears.

It was not possible to analyse this relaxation is detail but we were able to obtain the values of the activation parameters which are approximately $\Delta H^{\neq} = 10$ kcal mol^{-1} and $\Delta S^{\neq} = -35$ cal K^{-1} mol^{-1}. On the other hand, we must point out that in the t.s.d.c. studies of solid rotator phases which are being carried out in our laboratory, a relaxation between the order-disorder transition and the melting point is always observed. This finding is in agreement with many observations reported in the literature[4-6] and can be ascribed to the onset of the molecular self-diffusion or alternatively, to the existence of more than one solid rotator phase.

CONCLUSIONS

The molecular motions and the phase transitions of solid 2-adamantanone were studied by the technique of Thermally Stimulated Currents. A relaxation at -130 °C was observed which probably corresponds to the transition between the ordered phase and the solid rotor phase (or between the ordered phase and a biphasic system) and which is characterised by an activation enthalpy of $\approx$ 12.5 kcal mol^{-1} and an activation entropy of ≈ 22 cal K^{-1} mol^{-1}. Another relaxation was observed at higher temperatures, below the melting point, whose molecular nature is not yet completely understood but that can probably be ascribed to the onset of the molecular self-diffusion motions. The application of the t.s.d.c. technique to the study of molecular motions and phase transitions in molecular crystals showing solid rotator phases is at the very beginning. Nevertheless, the preliminary results obtained in the present study seem to indicate that this technique appears as a promising tool for such studies. More research work is being performed in our laboratory on different systems in order to evaluate the potential contribution of the t.s.d.c. technique in this field and in order to compare the obtained results with those obtained from other techniques.

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