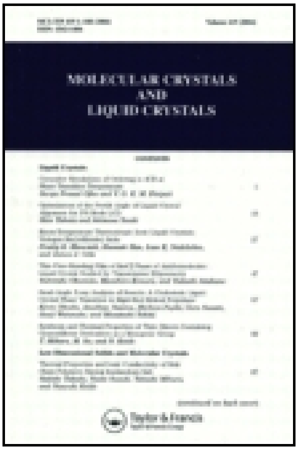

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Nuclear Magnetic Relaxation in Organic Crystals

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Nuclear Magnetic Relaxation in Organic Crystals

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Abstract—Nuclear magnetic relaxation in organic crystals is strongly influenced by processes of motion, such as the rotation of molecular substituents, the reorientation of molecules in the lattice, and the diffusion of molecules through the lattice. In company with studies of dielectric relaxation, heat capacity, and structure, nuclear magnetic resonance (NMR) experiments are valuable in examining these processes. In this paper, we review some advantages and limitations of the NMR method, and show correlations with other methods of studying molecular motions. NMR studies over a range of temperatures and moderate pressures are described for a variety of organic solids, including long-chain *n*-alkanes, planar molecules such as benzene, and nearly spherical molecules such as camphor and hexamethylbenzene.

The study of the organic solid state has benefited greatly in recent years from the contributions of nuclear magnetic resonance spectroscopy (NMR). This method has been particularly useful in detecting and distinguishing motions of molecules and their substituent groups in the solid. It provides information that complements the findings from other kinds of measurement, and in many cases it is the most direct view, at the molecular level, of processes of motion that underlie macroscopic properties. This review is intended to show examples of the scope of NMR in studies of the organic solid state, but with no attempt at completeness. More extensive information on the method and on the study of organic solids may be found in some recent review papers.[1-4]

Introduction

It is useful to visualize an experimental sample in NMR as consisting of two parts, the *spin system* and the *lattice*. The spin system is the ensemble of the nuclear magnets (e.g., protons) that the sample contains. The lattice is composed of the molecules that constitute the sample; the term implies a crystal, but it is used also for liquids and gases. The familiar experiments of chemistry are performed on the lattice. The NMR experiments are done in the spin system. It is valid to think of the spin system as having a temperature, T_S, which characterizes the Boltzmann distribution of the spin population among the energy states available to the magnetic nuclei. Similarly, the lattice is characterized by a temperature, T_L, which is the quantity that we measure with a thermocouple. The spin system and the lattice are weakly coupled, so at equilibrium the two systems are at the same temperature. However, it is easy to disturb the spin population by irradiating the sample with energy at the NMR frequency. The spin system can be made very hot ($T_S \gg T_L$), but the lattice is unaffected, because the heat capacity of the spins is extremely small. When the NMR irradiation is ceased, the spin population tends toward thermal equilibrium with the lattice. In the experiments of interest here, the equilibration occurs through fluctuating magnetic fields, generated by the thermal motion of magnetic nuclei attached to molecules or their substituent groups. The process is characterized by a time constant, T_1, the spin-lattice relaxation time. The process is most efficient (T_1 is shortest) when the spectrum of molecular motions contains a predominant component at about the NMR frequency, typically 10–100 Mc/sec. Thus, the appearance of a minimum in T_1 upon variation of the temperature or some other parameter marks the presence of some molecular motion characterized by a frequency in the range stated. There may be more than one minimum of T_1 over a span of experimental conditions. Each such minimum corresponds to a separate process of molecular relaxation. It is the burden of the investigator to find what molecular motion causes the observed nuclear magnetic relaxation.

In addition to these processes, there are important interactions among the nuclear magnetic dipoles. In a solid that is effectively free of motion, the magnetic field experienced by a given nucleus consists not only of the applied field of the laboratory magnet, but also the fields contributed by the magnetic moments of other nuclei in the neighborhood. These local fields amount to a few gauss, while the laboratory magnet typically supplies fields of the order of 10,000 gauss. Although modest in size, these local effects contribute significantly to the total field experienced by a given nucleus. They are composed of such a multiplicity of discrete interactions, some larger and some smaller, that effectively the resonance of a rigid solid consists of a broad envelope. The profile of this envelope is determined by the distances between the nuclei and the orientations of the internuclear vectors with respect to the applied field. That is to say, the shape of the resonance is determined by the structure of the solid; conversely, the structure can in principle be found from the line shape. In practice, however, it is impossible to carry out detailed determinations of this sort except in quite simple systems. Nevertheless, one can apply these molecular parameters to a calculation of the second moment or mean-square width of the resonance line,[5,6] and can test the merit of proposed structures through comparison with experiment.

When molecular motion develops at sufficient rate and amplitude, these couplings between nuclei tend to be averaged out, and the resonance envelope becomes narrowed. This change occurs when the frequencies of molecular motion becomes 10–100 kc/sec or greater. One can calculate the second moment expected for certain simple classes of motion,[6] for comparison with experiment.

To summarize, then, NMR experiments identify the presence of molecular motion in two portions of the frequency spectrum, 10–100 kc/sec and 10–100 Mc/sec, and they often provide structural information. In the next sections we give examples of the study of molecular motion in several kinds of organic solids. Comparisons are made with other classes of experiment and emphasis is given to the kinds of information for which NMR is a particularly effective source.

Molecular Rotation in the Solid

Pioneering studies of molecular motion in solid organic substances were carried out by Andrew[7,8] in investigations of polycrystalline benzene. This work showed the value of the NMR method, for with benzene and other nonpolar molecules the dielectric method of detecting molecular motion is of no avail. The NMR line is broad at low temperatures and becomes very much narrower at about 100°K. The second moment measured at low temperature, 10 gauss^2, coincides with the value calculated on the basis of the known crystal structure and with the assumption that the molecules are motionless. The measured second moment of the solid above 100 °K is 2 gauss^2, which corresponds to the value calculated for a lattice in which all the benzene molecules are rotating about their hexad axes. At the melting point of the solid, the line becomes very narrow and the second moment becomes very small. This early instance of the use of NMR on organic solids is a simple and clear-cut example of how this method gives direct information of molecular motion.

n-Alkanes

The *n*-alkanes constitute a group of compounds in which crystal structure and melting behavior are systematically related to molecular weight. It is now known, partly through NMR, that systematic features also occur in the molecular motion. Andrew[7] has calculated that the NMR second moment for an *n*-alkane, C_nH_{2n+2}, in a motionless lattice should be $26.3 + 19.1/(n + 1)$ gauss^2. His measurements on $C_{28}H_{58}$ and $C_{32}H_{66}$ at low temperatures agreed with these calculated values and supported the view that the lattices of these substances are essentially rigid under these conditions. He found, however, that the second moment for $C_{18}H_{38}$ at temperatures as low as 95 °K is smaller than would be expected for motionless lattices, and he concluded that some motion remains in these molecules even at these temperatures. More recent studies[9] have elaborated on the nature of molecular motion in solid *n*-alkanes. It is found that over a range of low temperatures one can distinguish the coexistence of stationary protons and protons in motion. Figure 1 shows the resonance for *n*-C_7H_{16} at 150 °K, measured as the derivative of the absorption with respect to magnetic field. The broad component of the resonance is ascribed to protons on the methylene segments of the molecule. The broadness shows that these groups are immobile at this low temperature. The narrow component indicates that part of the protons are in motion. This component is ascribed to the methyl groups, and it is inferred that these groups are rotating freely on the time scale that is important in measurements of the linewidth, i.e., on a scale which, in terms of frequency, is rapid compared with 10 kc/sec. This interpretation of the narrow component is borne out by the observation that the intensity decreases with increasing molecular weight in a series of *n*-alkanes, that is, with decrease in the relative abundance of methyl-group protons. As the temperature is lowered, the narrow component is found to merge into the broad component, and at 77 °K only a broad resonance is observed. This trend indicates that the rotation of methyl groups is quenched as the temperature is lowered. On the other hand, as the temperature is raised, the broad component of n-C_7H_{16} is abruptly narrowed at 182 °K, the melting point of the compound.

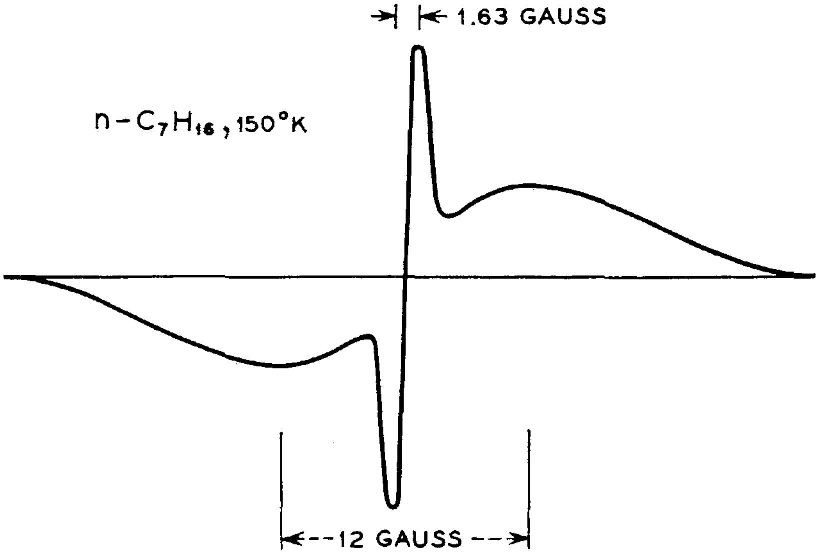

Figure 1. The derivative curve for n-C_7H_{16} measured at 150 °K (Ref. 9)

This information is extended in studies[9] of the spin-lattice relaxation time, T_1. Figure 2 shows the temperature dependence of T_1 in n-$C_{13}H_{28}$. The prominent T_1-minimum is ascribed to rotation of the methyl groups, and the occurrence of the minimum near 150 °K indicates that the spectrum of motions of the methyl group contains a predominant component near the NMR frequency, 50 Mc/sec, at this temperature. Below 150 °K and above, the spectrum is shifted, respectively, lower and higher in frequency than the distribution that yields the most effective relaxation. Accordingly, T_1 is increased in comparison to the most efficient relaxation. A different kind of motion enters a few degrees below the melting point and leads to a marked decrease in the spin-lattice coupling, that is, to a sharp drop in T_1. This change is ascribed[9] to the onset of rotational motion of the n-alkane chains, which has been observed in certain members of this series through macroscopic measurements.[10–12]

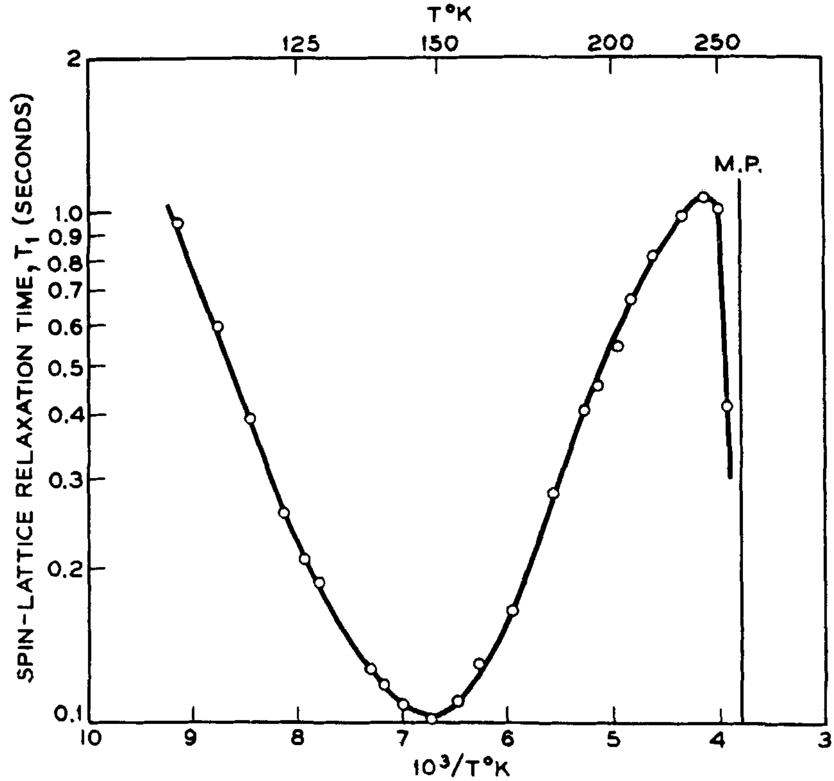

Figure 2. Temperature dependence of the spin-lattice relaxation time in n-$C_{13}H_{28}$ (Ref. 9).

The minimum in T_1 seen in Fig. 2 is observed at about the same temperature, 148° ± 5 °K, in n-alkanes from C_6H_{14} to $C_{40}H_{82}$.[9] The activation energy for the methyl rotation is found to be 2.6 ± 0.2 kcal/mole in all these compounds. The magnitude of T_1 at the minimum with increasing chain length is shown in Fig. 3. This trend reflects the mode of equilibration between the spin system and the lattice in these compounds. From the measurements of line shape and second moment, cited above, it is found that the methylene groups in these compounds are motionless at low temperature and are therefore ineffective in transfer of spin energy to the lattice. The methyl groups, however, are comparatively efficient in spin-lattice relaxation. It appears that the mechanism for dissipation of the spin energy of the methylene protons, following irradiation by the

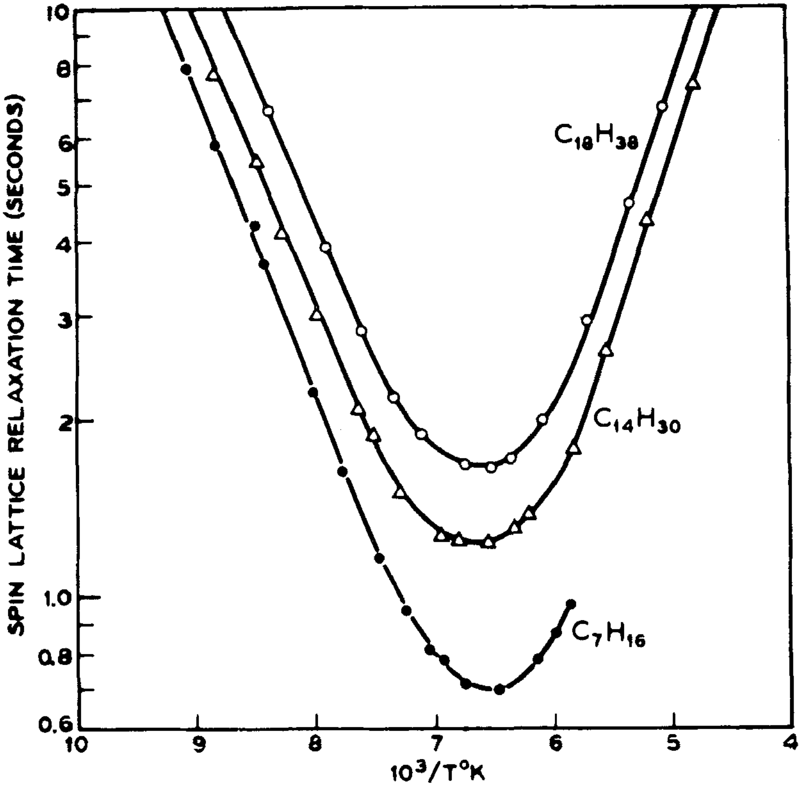

Figure 3. Temperature dependence of the spin-lattice relaxation time in n-C_7H_{16}, n-$C_{14}H_{30}$, and n-$C_{18}H_{38}$ (Ref. 9).

radiofrequency field, is the process of *spin diffusion*,[13–15] through which the energy of the methylene protons is transmitted to the methyl protons by spin-spin coupling. The efficiency of dissipation of the total spin energy in the molecule should therefore be related to the relative abundance of methyl groups: the greater the fraction of protons that are attached to methyl groups, the shorter should be the relaxation time. This expectation is borne out by measurements in a series of n-alkanes (Fig. 4).

Globular Molecules

The term "plastic crystals"[16] is loosely given to substances, usually organic, in which order in the crystal lattice is partly lost

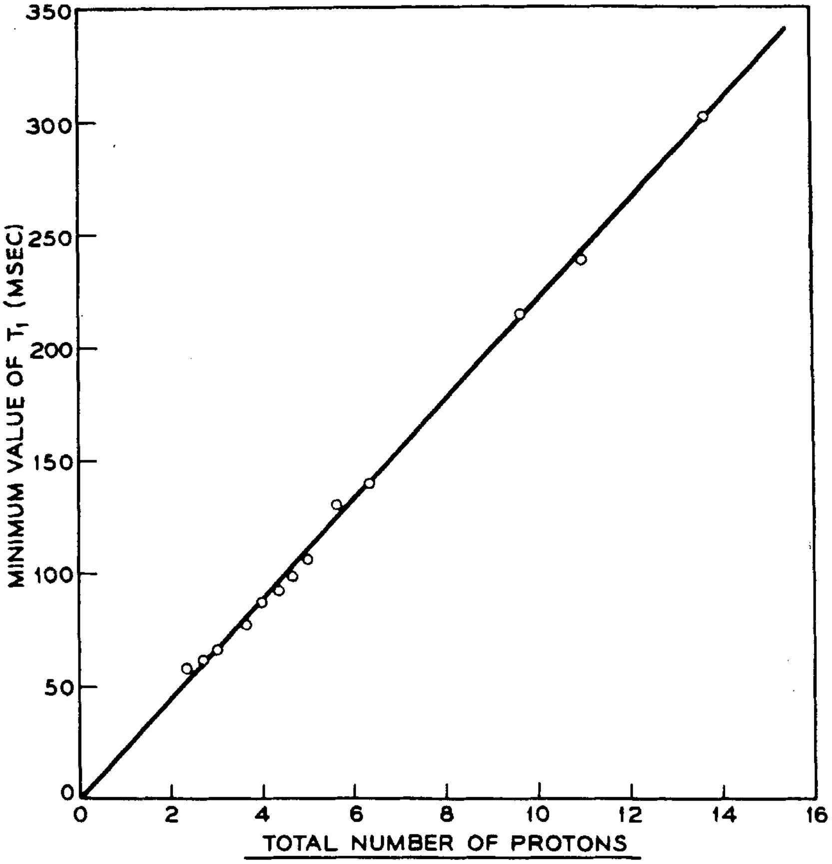

Figure 4. The methyl T_1 minimum value in the *n*-alkanes as a function of the relative number of methyl protons (Ref. 9).

through molecular motion. The compounds cited in the foregoing sections satisfy this description fairly well, but a conspicuous group is the broad class described as globular molecules. These substances consist of nearly spherical molecules that undergo reorientation in the solid state. NMR measurements have been made on a number of such substances.[2,3] A globular molecule that has been studied by many methods is camphor. A nearly spherical molecule, camphor exists as two optically active isomers. Natural camphor is the *d*-isomer, and synthetic camphor is a racemic mixture. The existence of molecular rotation in the solid has been shown in dielectric measurements,[17,20] studies of heat capacity,[21] and NMR experiments.[22,23] There is a transition in solid *d*-camphor at about 238 °K. Above this temperature is the so-called *rotator phase*, in which the molecules undergo rotational motion. Below this temperature the lattice is rigid. In solid solutions of *d*- and *l*-camphor, and particularly in the racemic substance, the transition to the rotator phase is much broader than in pure *d*-camphor. The effect of isomer composition on molecular motion in the transition region is seen clearly in Fig. 5. While the transition in *d*-camphor occurs sharply at 238 °K, the change in the racemic substance (0.5 mole per cent *d*-camphor) occurs over quite a broad interval of temperature.

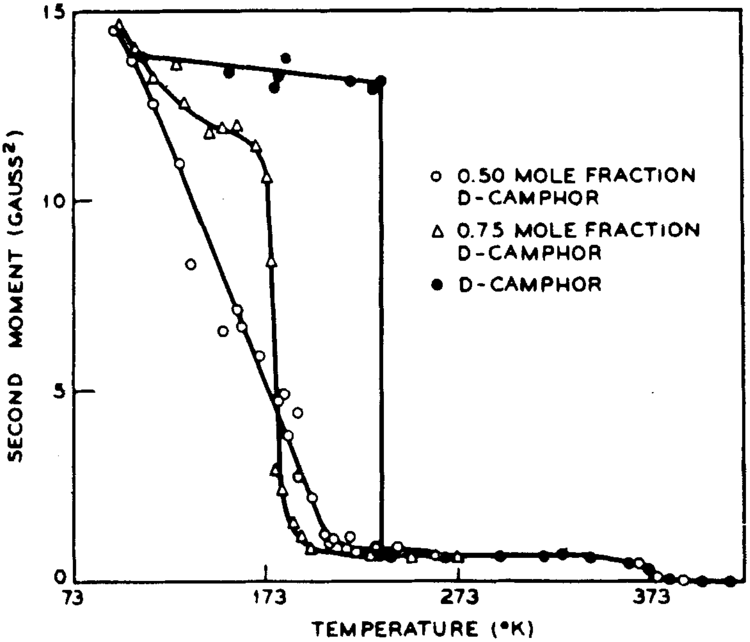

Figure 5. Temperature dependence of the NMR second moment in solid solutions of *d*- and *l*-camphor, and in pure *d*-camphor (Ref. 23).

For camphor in which the substituent methyl groups are rotating freely (on the time scale required for narrowing of the NMR absorption) but in which the lattice is otherwise motionless, the calculated value of the second moment[23] is 13 gauss^2. It is seen in Fig. 5 that the experimental second moments occur in this range at the lowest temperatures studied; indeed, the *d*-isomer exhibits a plateau at this value over an interval of some 50 °K. At the lowest temperatures studied, there appears to be an upturn in the second moment, presumably due to the quenching of rotation of the methyl groups with further decrease in temperature. Above the transition, in the rotator phase, the experimental second moments of all the samples are identical, 0.85 ± 0.15 gauss^2. This value is what would be expected if the molecules are tumbling about their centers of gravity. The decrease in the second moment near 360 °K is evidently due to self-diffusion in the solid.

The temperature dependence of the spin-lattice relaxation time in *d*-camphor is seen in Fig. 6. From the second moment data, Fig. 5, it is concluded that below 238°K molecular tumbling is essentially eliminated, at frequencies sufficient to produce line narrowing. Consequently the minimum in T_1 seen near 140 °K in Fig. 6 must be ascribed to a motion that is less constrained than molecular tumbling. Presumably this minimum is due to relaxation via the rotation of the three methyl groups in the camphor molecule. As was noted in the Introduction, a minimum in a T_1-temperature curve tells that the characteristic frequency of molecular motion is comparable to the NMR frequency at the temperature in question. We see in Fig. 6 that the position of the T_1-minimum is indeed shifted on the temperature scale according to the NMR frequency.

The theoretical curves in Fig. 6 were obtained through use of a theory due to Bloembergen, Purcell, and Pound.[24] The theory describes T_1 in terms of the internuclear distances, the NMR frequency, and the correlation time, τ_0, for the motion that produces the relaxation. Although the theory treats the motion in terms of only a single correlation time, it is nevertheless quite successful in describing the behavior of a wide variety of systems. The magnitude of T_1 at each of the minima is very well described by the theory if one takes the interproton distance of the methyl group to be the usual value, 1.79 Å. The dashed curves in Fig. 6 were calculated with the assumption[24] that τ_c has the form $\tau_c = \tau_c^0 \exp(\Delta E/RT)$ and that $\Delta E = 2.4$ kcal/mole, $\tau_c^0 = 6.6 \times 10^{-13}$ sec. The transition due to the onset of molecular tumbling is seen in Fig. 6 as an inflection near 240 °K. The small minimum in the T_1 curve at about 420 °K is ascribed to the self-diffusion process, noted previously in the measurements of the second moment. The effect occurs at higher

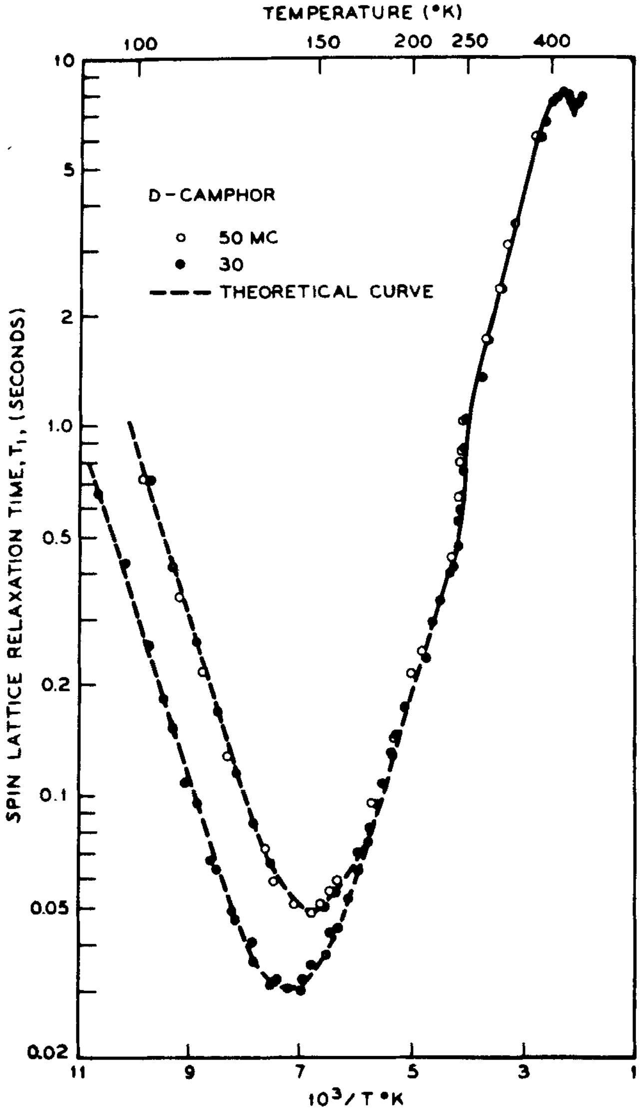

Figure 6. Temperature dependence of the spin-lattice relaxation time in *d*-camphor, measured at 30 and 50 Mc/sec (Ref. 23).

temperatures in the T_1 measurements than in the second moment studies, in keeping with the large difference in frequencies to which these two measurements are sensitive.

The spin-lattice relaxation of racemic camphor (Fig. 7) differs in

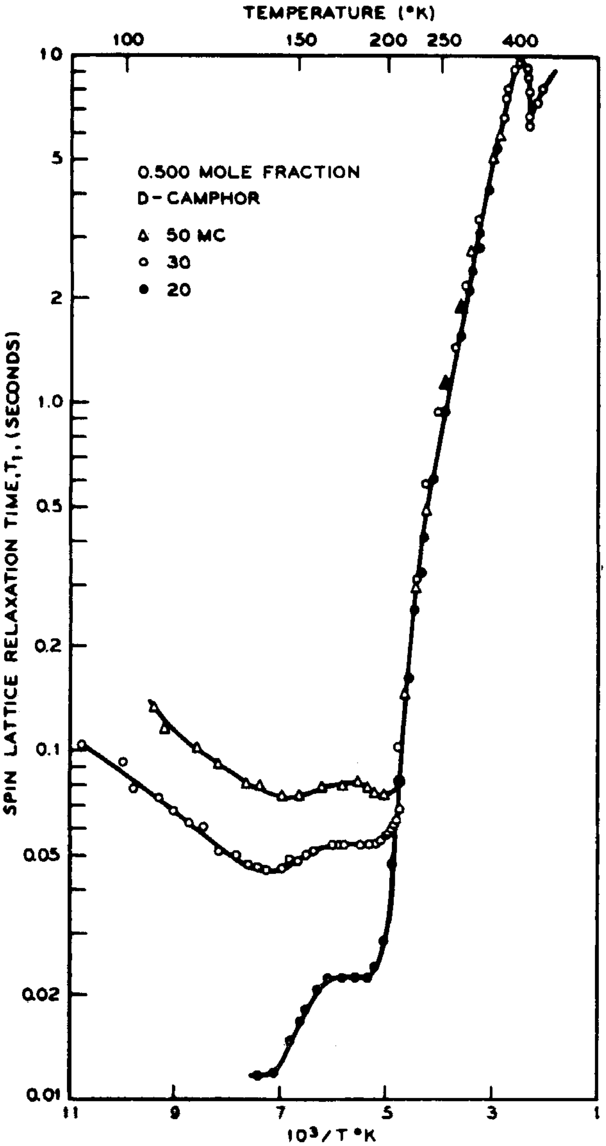

Figure 7. Temperature dependence of the spin-lattice relaxation time in racemic camphor (Ref. 23).

two ways from that of *d*-camphor below the transition temperatures: the curves are generally broader, and the absolute values of T_1 at the minima are greater than in the *d*-isomer. This behavior is characteristic of the existence of a distribution of NMR correlation times. The theory mentioned above is not appropriate to describe this relaxation in detail, although the fundamental physics still applies. Above the rotational transition temperatures the spin-lattice relaxation behavior is the same for *d*- and *dl*-camphor. Parenthetically, X-ray diffraction patterns for these two compounds are identical in the rotator phase, whereas they are quite different at low temperatures.[23] It is entirely reasonable that the rotator phases of the *d* and racemic compounds should be alike, for the *d* and *l* molecules ought to be indistinguishable when rotating at sufficient rate.

It is possible to divide the high-temperature data of Figs. 6 and 7 into separate contributions from molecular tumbling and self diffusion by assuming[25] that $1/T_1^{\mathrm{expl}} = 1/T_1^{\mathrm{tum}} + 1/T_1^{\mathrm{diff}}$. The contribution due to tumbling at the temperatures where diffusion appears in the observed T_1 (above ~375 °K) is found by extrapolation of the data between 275° and 375 °K. A graph of $\ln T_1^{\mathrm{diff}}$ versus $1/T$ yields a straight-line plot, from which an activation energy is obtained in the usual way. The value, 14.6 kcal/mole, is quite a bit larger than the values of 5–6 kcal/mole found for some substituted methanes,[25] and no doubt reflects the larger volume of the camphor molecule.

Effect of Hydrostatic Pressure

Although NMR studies have mostly been carried out at atmospheric pressure with temperature as the chief variable, the pressure dependence of nuclear magnetic relaxation is also of interest in studying factors that control molecular motion. Such studies[26–28] have been rather few in number, partly because of the difficulty of carrying out measurements at elevated pressure within the limited space of a magnet gap. The pressures employed in such work have in fact been quite modest compared with those used in other kinds of measurement. However, in organic solids such as plastic crystals one is able to see significant effects at pressures of only a few hundred atmospheres.

d-Camphor is known[29] to exhibit at least nine polymorphic modifications at pressures up to 50,000 atm. The temperature dependence of T_1 in two of these modifications[27] is shown in Fig. 8. It is seen that hydrostatic pressure affects the relaxation in the rotator phase, and

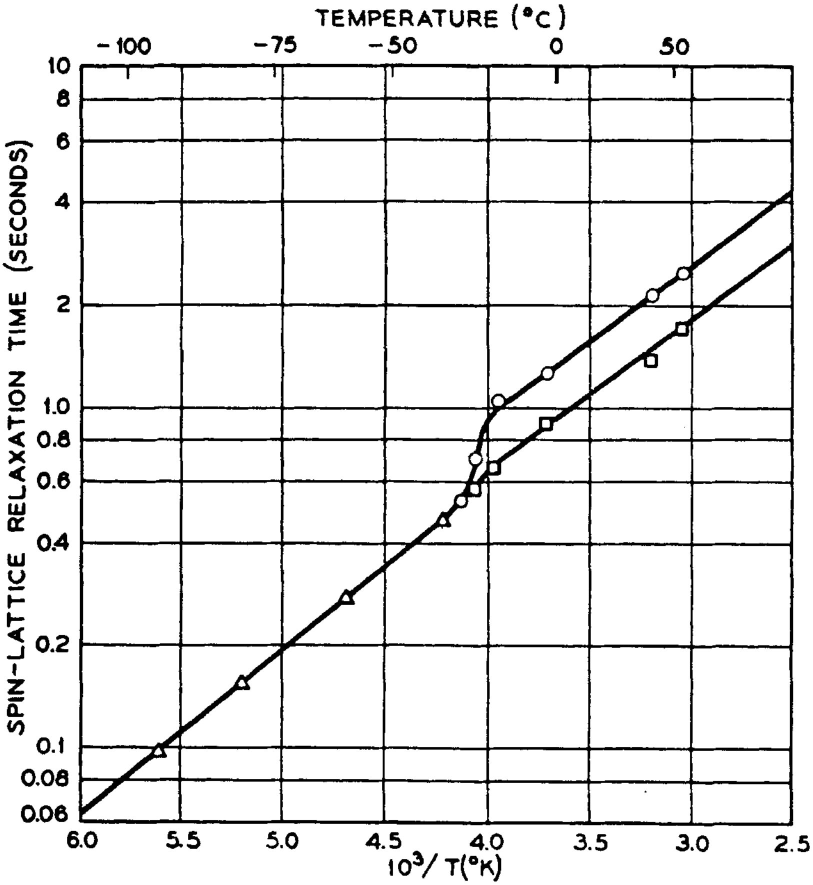

Figure 8. Temperature dependence of the spin-lattice relacation time in *d*-camphor. The data shown were taken under hydrostatic pressures of 1 and 680 atm. ○, 1 atm; □, 680 atm; △, pressure independent (Ref. 27).

shifts the transition temperature upward. The modest pressures used in this work, up to 680 atm (10,000 lb/in^2), produced no detectable change in the relaxation of the rigid phase. In racemic camphor, however, the behavior is quite different[27] (Fig. 9). As was noted earlier, the change involving quenching of rotation in *dl*-camphor occurs over a broad range of temperature. At temperatures *below* the lower limit of this quenching interval, 208 °K, it is found that application of pressure (680 atm) causes the T_1-temperature behavior to follow the middle curve in Fig. 9 on cooling and the

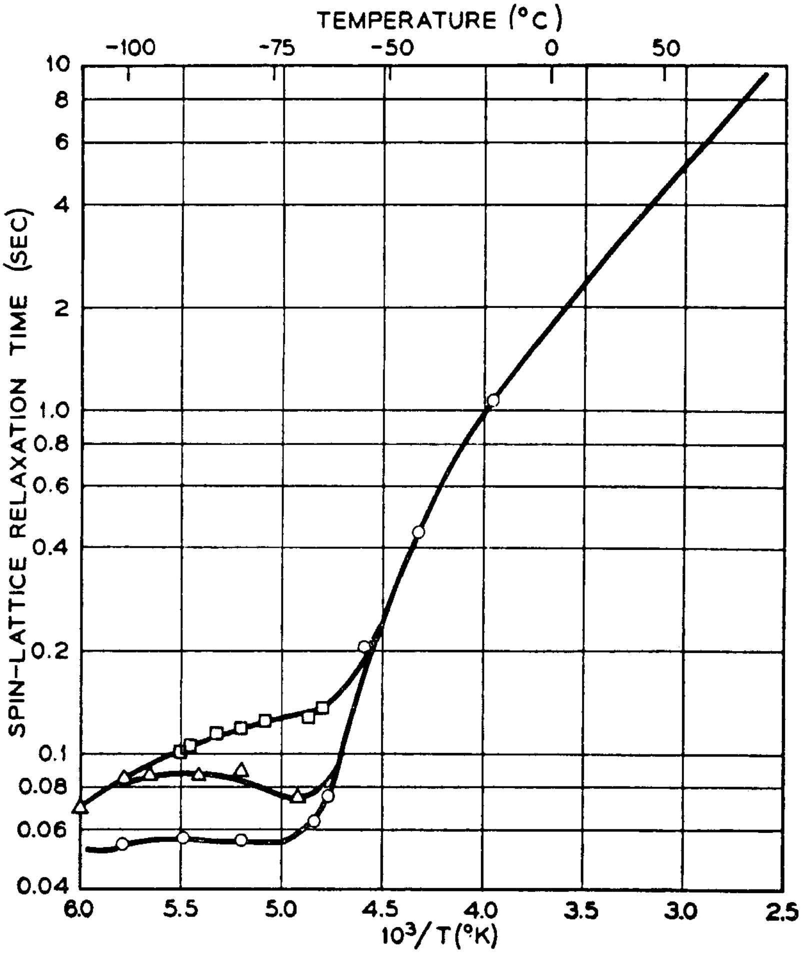

Figure 9. Temperature dependence of the spin-lattice relaxation time in racemic camphor. The three branches of the curve at lower temperatures were observed under conditions described in the text. ○, 1 atm; △, 680 atm (cooling); □, 680 atm (warming) (Ref. 27).

upper curve on warming. If pressure is applied in the rotator phase (specifically, above 225 °K), the relaxation follows the upper curve on both cooling and warming. It should be noted that the successively higher curves, produced by choice of pressure and temperature cycles, are tending toward the T_1's found with *d*-camphor, in which the low-temperature phase is a well-ordered crystalline structure that is

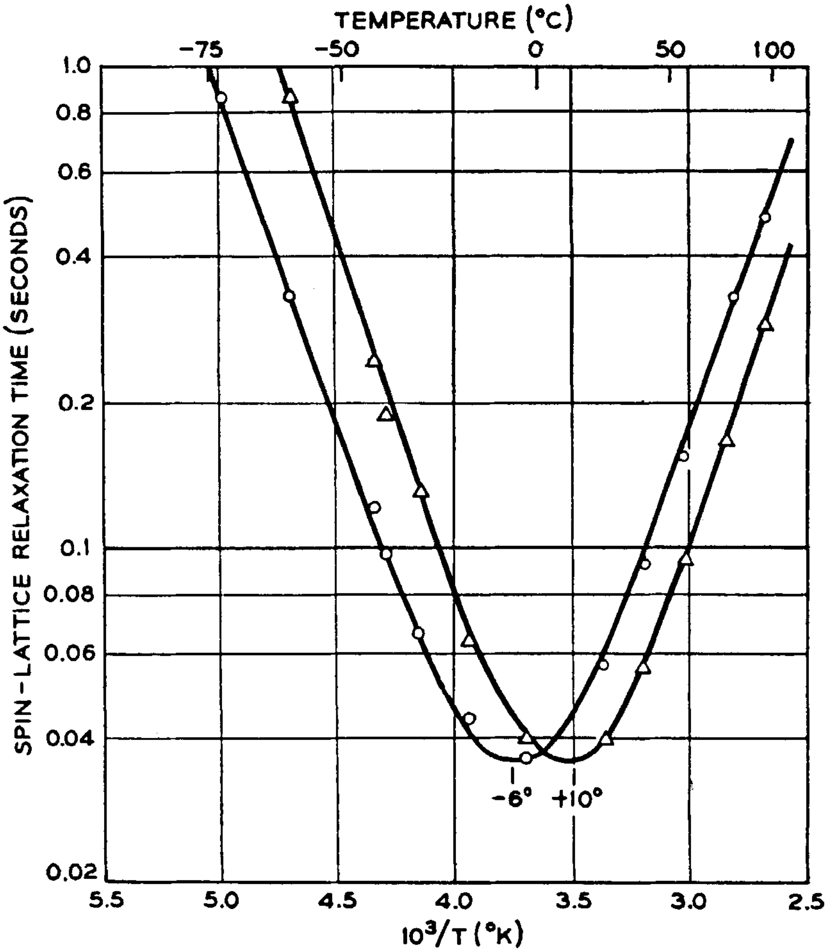

Figure 10. Temperature dependence of the spin-lattice relaxation time in solid hexamethylbenzene, measured under hydrostatic pressures of 1 and 680 atm. ○, 1 atm; △, 680 atm (Ref. 27).

insensitive to moderate variation in pressure. The shift toward longer T_1's in Fig. 9 reflects a decrease in molecular motion. It appears, therefore, that this trend consists of a pressure annealing, in which there is a progressive reduction in the number of lattice defects during cycling.

The temperature and pressure dependence of nuclear magnetic relaxation can be used to give a phenomenological description of the

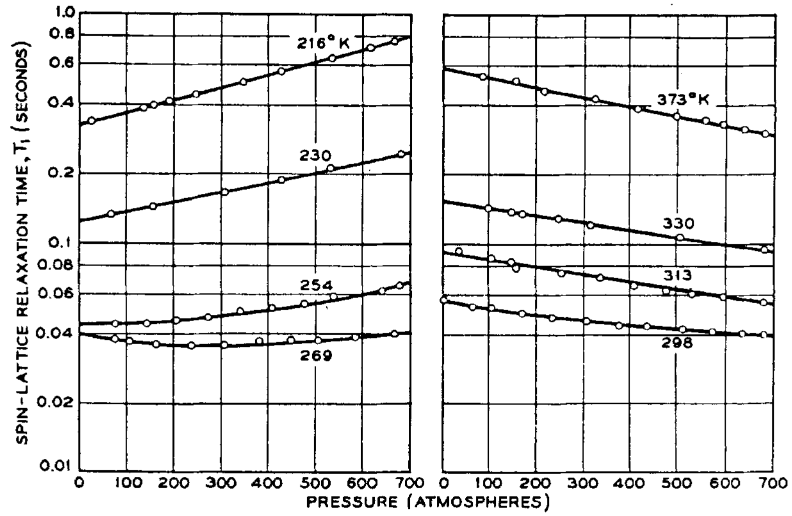

Figure 11. Pressure variation of the NMR spin-lattice relaxation time in solid hexamethylbenzene at eight different temperatures (Ref. 27).

TABLE 1 Enthalpies and Volumes of Activation

Compound	ΔH^* (kcal/mole)	V^* (cm^3/mole)	V_M (cm^3/mole)
Camphor (rotator phase)	2.8	14.5	152
Benzene	4.0	15.2	89
Hexamethylbenzene	6.4	21.3	162
CH_3 rotation (n-alkanes)	2.6	<2	15

motion as a thermally activated process. It is commonly found that semilogarithmic plots of T_1 with respect to $1/T$ are linear over fairly wide regions of temperature. The enthalpy of activation can then be described as $\Delta H^* = R[\partial \ln T_1/\partial(1/T)]_P$. Figure 10 shows data for a globular molecule, hexamethylbenzene, measured at two pressures. The linear segments of these curves yield values of $\Delta H^* = 6.8$ kcal/mole at 1 atm pressure and 6.4 kcal/mole at 680 atm. Within experimental error ΔH^* is independent of pressure.

Similarly, from relaxation measurements at various pressures, the volume of activation is described as $\Delta V^* = RT(\partial \ln T_1/\partial P)_T$. Figure

11 shows a set of curves for hexamethylbenzene, taken at different temperatures over a range of pressures. These isotherms are linear except at temperatures near the T_1-minimum. The linear isotherms can be used to calculate ΔV^*. Table 1 lists some activation parameters obtained through this approach. Also shown are the molar volumes, V_M. It is seen that $\Delta V^*/V_M = 0.10$–0.15 for these solids. This range of values is about the same as that which was found in NMR measurements of the self-diffusion of normal and branched alkanes in the liquid state.[30]

Concluding Remarks

This brief account of the use of NMR to study some organic solids is obviously only a fragmentary view, but the great scope of the method to study structure and motion should be evident. Not mentioned in this account is the extensive use of NMR for a major class of organic solids, the high polymers. Considerable insight into the physical properties of these complex substances has been gained through NMR.[31–33] The application of these methods to other kinds of organic solids, particularly with the use of elevated pressure and wide ranges of temperature, will contribute greatly to a critical understanding of the physical behavior of these compounds. A new development in the NMR method, the use of rotating-frame nuclear magnetic relaxation,[34] is found to extend the range of measurement to very slow motions and has already been applied to several organic compounds[35–37] and some polymers.[38,39]

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