Molecular Reorientation and Self-Diffusion in Solid Cubane by Deuterium and Proton NMR

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Deuterium and proton NMR line shape and relaxation measurements are reported for the *sym*-cubane-d_2 isotopomer (D_{3d} symmetry) in the temperature range from 200 K to the melting point of the solid. The results confirm the polymorphic phase sequence: solid II $\xrightarrow{394\text{K}}$ solid I $\xrightarrow{405\text{K}}$ liquid, reported earlier by White et al. The deuterium spectrum below 215 K exhibits a Pake doublet corresponding to an axially symmetric quadrupole coupling tensor with a coupling constant of $Q_c = 178$ kHz. Above this temperature the spectrum develops features characteristic of the onset of dynamic processes leading to a single line at about room temperature. Longitudinal relaxation time measurements show a T_1 minimum at 344 K. On transition to solid I there is a discontinuous narrowing of the line and a concomitant increase in T_1. These results are quantitatively interpreted in terms of reorientational jumps of the cubane molecules between their various equivalent orientations. The jump rate *k* in solid II follows an Arrhenius behavior over a range of almost seven decades with an activation energy $E = 62$ kJ mol^{-1}. Transition to solid I results in a discontinuous increase of *k*. Proton line width measurements in solid II show two motional narrowing steps. The first, at around 240 K, is due to the cubic jumps while the second, at around 375 K, corresponds to molecular self-diffusion between the lattice sites. The activation energy for this process is $E_d = 83$ kJ mol^{-1}. On transition to solid I there is also a discontinuous increase in the rate of this process. The proton T_1 values are predominantly affected by the reorientation process and are consistent with the deuteron data. At temperatures above 340 K, where the deuterium NMR spectrum is expected to be a single Lorentzian with a width of less than 400 Hz, it actually exhibits, in both phases II and I, a Pake doublet corresponding to an axially symmetric quadrupole coupling tensor with a very small coupling constant $Q'_c = 0.48$ kHz. This indicates that the reorientation process is not perfectly cubic. Possible reasons for this surprising effect are discussed.

Introduction

Cubane (C_8H_8) is one of the three molecules with Platonic structure that can be chemically synthesized.[1] It was first prepared by Eaton and Cole in 1964[2] and has since been the subject of extensive studies with regard to its physical and chemical properties and as an intermediate moiety in organic synthesis.[3,4] Unsubstituted cubane crystallizes at room temperature in the space group $R\bar{3}$ with the cell constants $a = 5.340$ Å, $\alpha = 72.26°$ and one molecule per unit cell.[5] Projections of the crystal structure and of a single cubane molecule are shown in Figure 1. Within the experimental accuracy of the X-ray measurements,[5] the molecules have cubic (O_h) symmetry. In the crystal they align with one of their main body diagonals along the crystallographic S_6 axis. A detailed analysis of the vibrational spectrum of (isotopically) normal cubane and of four of its deuterated isotopomers, including cubane-d_1 (with C_{3v} symmetry), *sym*-cubane-d_2, *sym*-cubane-d_6 (D_{3d}), and cubane-d_8 (O_h) in the solid state and in solution, was carried out by Della et al. using infrared and Raman spectroscopy.[6] It is noteworthy that although the spectra of the d_0 and d_8 isotopomers in solution follow the selection rules for O_h symmetry, in the solid they correspond to S_6, reflecting the local symmetry in the crystal rather than that of an isolated molecule. The Raman results (for C_8H_8) were confirmed by Cole et al.,[7] who have also investigated the vapor phase infrared spectrum of cubane. A subsequent temperature dependence Raman study by Dalterio and Owens[8] indicated the onset of order−disorder fluctuations above room temperature and a solid−solid phase transition (by DSC) at about 10 K below the melting point. They suggested that the high temperature solid is an orientationally disordered plastic phase.

More recently, the thermodynamic parameters as well as the reorientation kinetics in solid cubane were investigated by White et al.[9] using calorimetry and ^{13}C NMR. Their results clearly show that cubane is polymorphic with the following phase sequence

$$\text{solid II} \xrightarrow[(5.94)]{394\text{ K}} \text{solid I} \xrightarrow[(8.7)]{405\text{ K}} \text{liquid}$$

where the numbers in parentheses correspond to the transition enthalpy in kJ mol^{-1}. The crystal structure quoted above ($R\bar{3}$) corresponds to solid II; that of solid I has so far not been determined. The ^{13}C T_1 measurements indicate rapid molecular reorientations already well below room temperature in solid II. For this phase, White et al. found an Arrhenius behavior for the rate *k* of this process, with an activation energy $E = 58 \pm 6$ kJ mol^{-1}. This result agrees with that obtained by Raman scattering.[8]

In the present work we extend the investigation of the dynamic properties of cubane, using proton and deuterium NMR of a *sym*-cubane-d_2 sample. There are several reasons for extending the ^{13}C results. Firstly, since the earlier NMR

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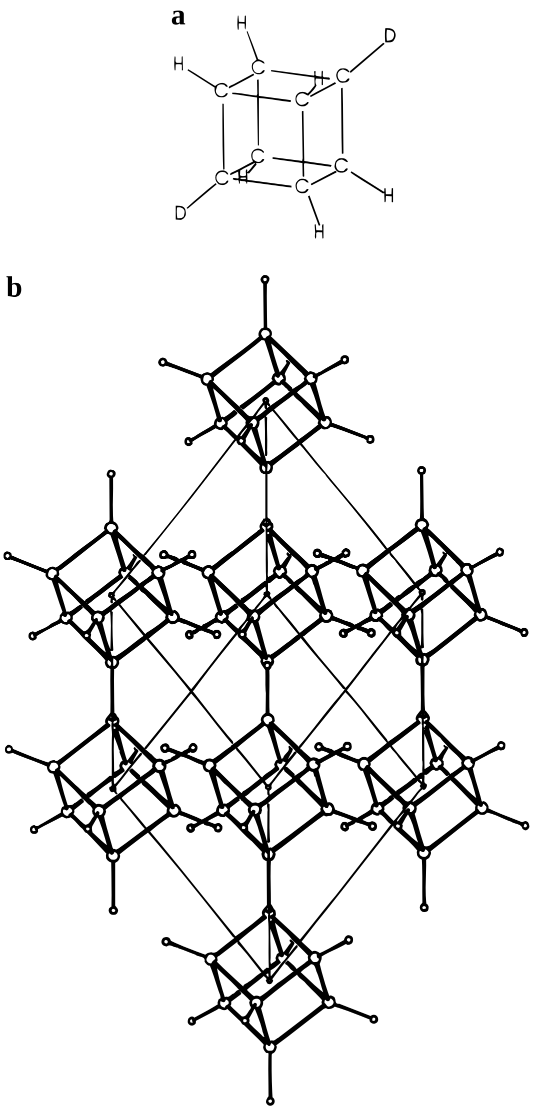


Figure 1. (a) Perspective view of the cubane molecule. (b) Rhombohedral unit cell of the solid II crystal.

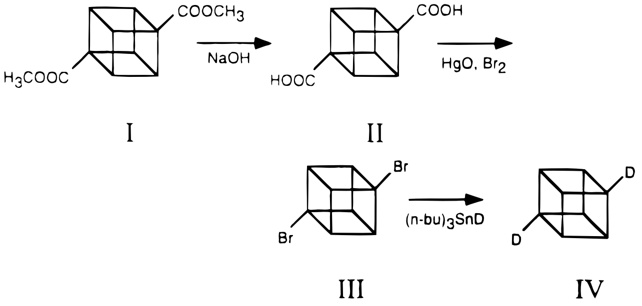
experiments were limited to solid II, we deemed it interesting to extend the investigation to solid I. Secondly, relaxation studies alone, although they provide reliable kinetic parameters for the dynamic processes, are usually not very sensitive to the detailed mechanism of the reaction. In the case of cubane, it is natural to assume (as do White et al.) that the process consists of reorientational jumps between equivalent molecular orientations. In the present work we have actually verified this mechanism by a detailed line shape analysis of deuterium NMR spectra of the cubane-d_2 sample. To extend the measurements of the rate k of this process to a larger temperature range, we performed deuteron and proton T_1 measurements in both solid phases.

While both ^{13}C and ^{2}H spectra are highly sensitive to molecular reorientations, they are very little so to translational self-diffusion. On the other hand, the ^{1}H NMR spectrum is also affected by the latter process. In a rigid solid, the width of this spectrum has contributions, of similar order of magnitude, from intra- and intermolecular dipolar interactions. Molecular motions will average out these interactions. However, while the intramolecular interactions are predominantly affected by reorientations, the intermolecular ones are mainly sensitive to self-diffusion, thus providing a means to probe it. Therefore, we have measured the temperature dependence of the width of the ^{1}H NMR line in cubane, finding a two-step narrowing with increasing temperature, the second step being clearly related to self-diffusion.

An unexpected feature in the deuterium NMR spectrum was observed above ~340 K in both solid phases. In this temperature range, instead of a sharp Lorentzian line, the deuterium spectrum exhibits a Pake doublet with a very small quadrupole coupling constant of 0.48 kHz. Very likely, this residual interaction also exists at lower temperatures, but is masked by the larger line width. For solid II this behavior can be explained in terms of an isotope effect on the orientation of the main diagonal D−D axis relative to the S_6 crystallographic axis. If solid I is cubic, as we suspect, the effect in this phase must correspond to a remarkable cooperative alignment of the D−D axes in the otherwise cubic lattice.

Experimental Section

Material. *Sym*-cubane-d_2 was prepared from the corresponding *sym*-cubanedicarboxylic acid dimethyl ester (I) by a series of steps involving saponification of the ester, bromination, and debromination by deuterium as described in the scheme below.



The starting compound (I) was obtained from Drs. U. Romano and C. Neri (EniChem Synthesis, Milano). Five grams of I were refluxed and stirred with 100 mL of a 10% aqueous NaOH solution for 1.5 h. After cooling, the mixture was acidified with concd HCl, and the resulting precipitate, *sym*-cubanedicarboxylic acid (II), was filtered and dried under vacuum; yield 3.6 g.

To a refluxing mixture containing 3.06 g of II, 7.8 g of red mercury oxide, and 40 mL of CH_2Br_2 was dropwise added a solution of bromine (6.4 g in 20 mL of CH_2Br_2) under constant stirring. The mixture was kept at 80−90 °C for 2.5 h, cooled, and filtered, and the filtrate was evaporated under vacuum at 40 °C. The residue was extracted five times with hexane and the solvent evaporated, yielding 2.5 g of crude *sym*-cubane-Br_2 (III) (mp 180−182 °C). After sublimation at 80 °C/10^{-5} torr, pure III (mp 187−189 °C) was obtained. (Caution: While attempting sublimation at a temperature higher than 80 °C, a violent explosion occurred during the present synthesis, probably due to the catalytic effect of residual traces of mercury salts in the crude product. Therefore, it is advisable to keep the temperature during sublimation at or below 80 °C.)

To obtain *sym*-cubane-d_2 (IV), 1 g of III was mixed with 3 g of tri-*n*-butyltin deuterate (Aldrich) and a few milligrams of azoisobutyronitrile (2,2′-azobis-2-methylpropiononitrile). The mixture was stirred in a closed vial and irradiated with UV light from a mercury high pressure lamp (water filter) placed at a distance of 40 cm from the reaction vessel. After 30 min of irradiation, the vial was heated to 80 °C for a few minutes, followed by several hours of room temperature UV irradiation as before. The process was discontinued only after a cooled sample from the reaction mixture did not show crystals of III under polarizing microscopy examination. The reaction vessel was then connected to a manifold, cooled with liquid nitrogen, and evaporated. The closed system was warmed to room

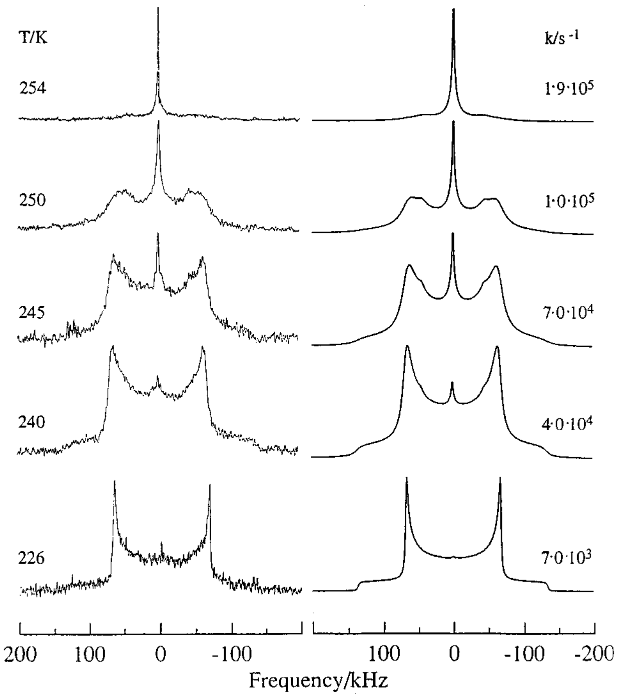


Figure 2. Left: Temperature dependence of experimental quadrupole echo spectra of the *sym*-cubane-d_2 sample. The 90° pulse width was 2.2 μs, the time interval between the pulses in the quadrupolar echo sequence 20 μs. Right: Simulated lineshape calculated for $Q_c = 178$ kHz, $1/T_2 = 400$ s^{-1}, and the indicated jump rate constants.

temperature and the solid content sublimed into another flask which was kept at -196 °C. The sublimation procedure was repeated several times until white crystallites of *sym*-cubane-d_2 were obtained. Yield 0.33 g; $m/e = 105$, 104 $[\mathrm{M} - \mathrm{H(D)}]^{\oplus}$ base peak; single proton NMR line at $\delta = 4.0$ ppm. Differential scanning calorimetry (DSC) measurements on the cubane-d_2 sample gave, within experimental errors, the same transition temperatures and transition enthalpies as determined by White et al. by the same method.[9] This rules out any significant deuterium isotope effect on the thermodynamic parameters of cubane, as found, e.g., by Wasylishen et al. in the case of norbornane.[10]

NMR Measurements. Deuterium NMR spectra were recorded on a Bruker CXP300 spectrometer at a frequency of 46.07 MHz at the Weizmann Institute and on a home-built 72.1 MHz spectrometer at the Max-Planck-Institute. Both quadrupole echo and single pulse FID signals were recorded, followed by Fourier transformation. The proton measurements were performed on the CXP300 spectrometer at 300 MHz by single pulse excitation.

Results and Discussion

Deuterium Dynamic NMR Lineshape Measurements. Examples of deuterium NMR spectra obtained from the cubane-d_2 sample in the temperature range 220 K to 260 K are shown in Figure 2. Starting from a rigid powder spectrum at 220 K, the spectra develop typical dynamical features when the temperature is increased, which gradually evolve into a single sharp peak above ~250 K. The low temperature spectrum corresponds to an axially symmetric quadrupole coupling tensor with a quadrupole coupling constant $Q_c = e^2qQ/h = 178$ kHz. The evolution of the spectrum above 230 K, in particular the convergence to a single line at higher temperatures, is consistent with a cubic jump model. By a "cubic jump model" we mean that, in the course of time, the molecules occupy all symmetry-related orientations of the cube, with equal average residence time between jumps, and that the deuterium quadrupole coupling tensors in the various sites are related by the corresponding symmetry operations. The convergence to a single line at high jump rates does not, by itself, constitute a proof for this mechanism, since, e.g., random isotropic diffusion, or large angle jumps, will also lead to a single-line spectrum. However, the line shapes in the intermediate regime (230 K to 250 K), in particular the appearance of the singularities at the center of the spectra, provide strong evidence for the former mechanism.[11] The isotropic reorientation mechanism can, of course, also be ruled out on the basis of the X-ray data, since it would lead to complete orientational disorder, contrary to the crystallographic results for solid II. We shall see further below that the reorientational jumps in the *sym*-cubane-d_2 sample deviate slightly from perfect cubic symmetry, but for now we shall disregard this small effect.

To simulate the dynamic deuterium NMR spectra according to the cubic jump model, we applied known procedures in which the effect of relaxation and exchange during the quadrupole echo sequence are included.[12] Because of the inversion symmetry of the cube, the eight-site problem reduces to a four-site one. It is thus sufficient to consider only four deuterons at the corners of an enclosed tetrahedron. To set up the dynamic matrix it may appear on first glance that it would depend on whether the jumps involve rotation about the C_4, C_2, or C_3 axes of the cubane molecule. If, however, one assumes that the reorientation probability about the three C_4 axes is the same and likewise the reorientation probability about the six C_2 or the four C_3 axes, the various mechanisms lead to equivalent dynamic matrices, differing only by scalar coefficients. Analysis of the possible mechanisms yields the following dynamic matrix

$$R = k\begin{pmatrix} -1 & {}^1/_3 & {}^1/_3 & {}^1/_3 \\ {}^1/_3 & -1 & {}^1/_3 & {}^1/_3 \\ {}^1/_3 & {}^1/_3 & -1 & {}^1/_3 \\ {}^1/_3 & {}^1/_3 & {}^1/_3 & -1 \end{pmatrix} \qquad (1)$$

where k is $3/(4\tau_3)$, $1/\tau_4$, $1/(2\tau_2)$, or $1/\tau'_2$, depending on whether the reorientations correspond to C_3^1, C_4^1, C_2^1, or C_4^2 rotations, and τ_n is the corresponding correlation time (mean lifetime between jumps).

With this dynamic matrix, we simulated spectra matching the experimental ones as closely as possible, taking k and an exchange independent transverse relaxation rate, $1/T_2$, as the only adjustable parameters. Examples of such simulated spectra are shown in the right column of Figure 2. It may be seen that they faithfully reproduce the experimental results, including in particular the singularity at the center frequency. This singularity is typical of cubic jumps[11] and corresponds to those molecules in the powder which lie parallel to the external magnetic field with one of their C_4 axes. For such molecules the deuterium spectrum of all sites is a singlet falling at the center of the spectrum, since the unique principal quadrupole coupling tensor directions (the C−D bond directions) of all deuterons are inclined by the magic angle, $\pm\theta = \pm\cos^{-1}(1/\sqrt{3})$, to the external field. Cubic jumps therefore do not modulate the resonance frequency, hence the signal remains sharp. By fitting the calculated spectra to the experimental results visually, the rate constants k for the jump process were derived. The corresponding correlation times, $\tau = k^{-1}$, are plotted in Figure 3 with the symbol □ vs the reciprocal absolute temperature.

Deuterium Longitudinal Relaxation Time Measurements. To extend the temperature range of the kinetic results presented

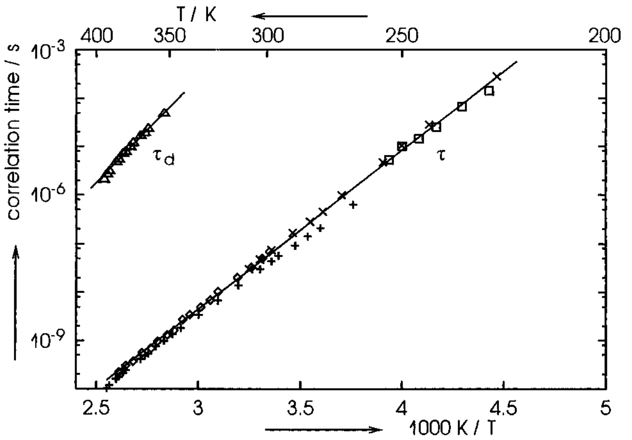


Figure 3. Arrhenius plot of the correlation times for the cubane reorientation, τ, and self-diffusion, τ_d, in solid II, obtained from different experiments. The symbols indicate results from: □ deuterium lineshape analysis; × deuterium T_1 at 72.1 MHz; ◇ deuterium T_1 at 46.07 MHz; + proton T_1 at 300 MHz, △ proton linewidth.

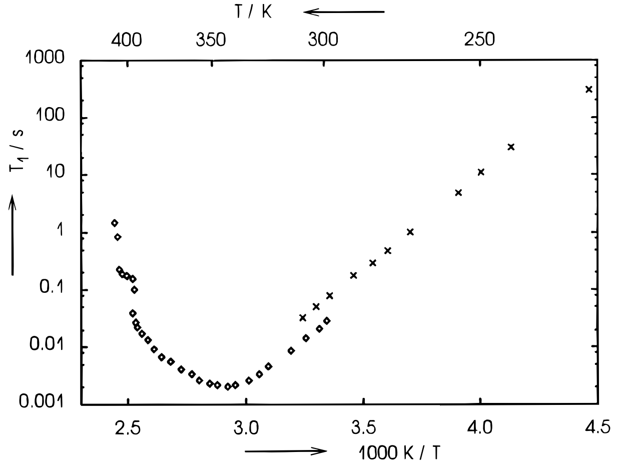


Figure 4. Plots of the deuterium longitudinal relaxation time of *sym*-cubane-d_2 measured at 46.07 MHz (◇) and 72.1 MHz (×) vs the reciprocal absolute temperature.

above, measurements of the longitudinal relaxation time T_1 were carried out between 225 K and the melting point of the cubane-d_2 sample, at both 72.1 MHz (between 225 K and 308 K, using saturation recovery) and at 46.07 MHz (between 300 K and the melting point, using inversion recovery). Within the experimental accuracy the build-up of the magnetization was exponential at all temperatures. The derived relaxation times are plotted vs the reciprocal absolute temperature in Figure 4. The data for 46.07 MHz exhibit a T_1 minimum at 344 K in solid II and clear discontinuities at the temperatures corresponding to the transitions solid II → solid I and solid I → liquid. Within the solid II range, the T_1 results can quantitatively be interpreted in terms of the BPP equation[13]

$$\frac{1}{T_1} = \frac{2}{15}\left(\frac{3}{2}\pi Q_c\right)^2\left[\frac{\tau}{1+\omega_0^2\tau^2} + \frac{4\tau}{1+4\omega_0^2\tau^2}\right] \qquad (2)$$

Although this equation applies strictly to random isotropic reorientations, it is almost indistinguishable from that expected for cubic jumps.[14] Longitudinal relaxation times at 72.1 MHz were only measured at low temperatures where $\omega_0\tau \gg 1$, so that no minimum was observed. Where measurements at both frequencies are available at the same temperatures, the results are within the expected ratio of $T_1(72.1)/T_1(46.07) = (72.1/46.07)^2 = 2.45$. From eq 2, the T_1 minimum is expected at $\omega_0\tau = 0.6158$, so that with the observed value of T_1 (minimum) = 2.17 ms (at $\omega_0/2\pi = 46.07$ MHz) a quadrupole coupling constant of $Q_c = 177$ kHz can be calculated, in excellent agreement with the value derived from the low temperature spectra. The correlation times derived from the T_1 results in solid II are also plotted in Figure 3 (symbols ◇ for 46.07 MHz and × for 72.1 MHz). They agree perfectly well with those obtained from the line shape analysis, yielding an overall Arrhenius equation for the reorientation rate

$$k = k^0 \exp(-E/RT), \qquad (3)$$

where $E = 62$ kJ mol^{-1} and $k^0 = 1.1 \times 10^{18}$ s^{-1}, in reasonable agreement with the values obtained earlier by White et al. from ^{13}C data.[9] Note that the value of k^0 is too large by orders of magnitude for identifying k^0 with an "attempt frequency" of any kind.

As indicated before, the experimental results do not provide information on whether the cubane molecules reorient by two-, three-, or four-fold jumps. Theoretical calculations of the barriers for the various single-particle reorientations of cubane in solid II were carried out by Fyfe and Harold-Smith,[15] who found the lowest value for the C_4 jumps. If this mechanism is indeed the one which nature prefers, τ in eq 2 should be identified with τ_4 of the previous section. The discrepancy between the calculated barrier height, 35 kJ mol^{-1}, and the experimental value has been discussed by White et al.[9]

The temperature range of solid II is too narrow to derive the corresponding kinetic parameters for this phase from T_1 data. However, from the discontinuous increase in T_1 at the transition to solid I an increase by a factor of 10 in the reorientation rate may be estimated, with $k \approx 8 \times 10^{10}$ s^{-1} at the midpoint of this phase. Transition to the liquid phase yields another discontinuous increase in k to about 4×10^{11} s^{-1} at the melting temperature.

Proton Line Width and T_1 Measurements. The deuterium results described in the previous two sections provide information on the reorientation rate of the cubane molecules in both solid phases. Deuterium NMR is, however, usually not suitable for measurements of translational self-diffusion, since its spectrum is almost unaffected by intermolecular interactions. The situation is quite different for proton NMR, where the dominant anisotropic term in the spin Hamiltonian is the dipolar coupling between all protons in the system, including intra- and intermolecular interactions with comparable contributions to the static line width (or second moment). Pure molecular reorientations will average out the intramolecular dipolar interactions, while self-diffusion will in addition also average out the intermolecular ones.

To check whether self-diffusion can be detected in cubane, we have measured the proton NMR line width $\delta\nu$ (full width at half maximum height) in the cubane-d_2 sample over the temperature range from 190 K to the melting point. The results, which clearly show the effects of two dynamic processes, are summarized in Figure 5. Below 230 K the system is rigid and the observed line width (47 kHz) reflects the full intra- and intermolecular dipolar interactions between the protons in the sample. Above 230 K the molecular reorientation rate becomes comparable with the intramolecular dipolar interactions resulting in the latter being averaged out and the line width being concomitantly reduced, until a new plateau at 11 kHz is reached. This line width reflects solely the intermolecular dipolar interactions in a lattice consisting of rapidly reorienting cubane-d_2 molecules. Above 350 K a second averaging process sets in, which results in a gradual reduction in the line width, down to 1 kHz just below the solid II → solid I transition temperature. This process evidently averages out the intermolecular dipolar

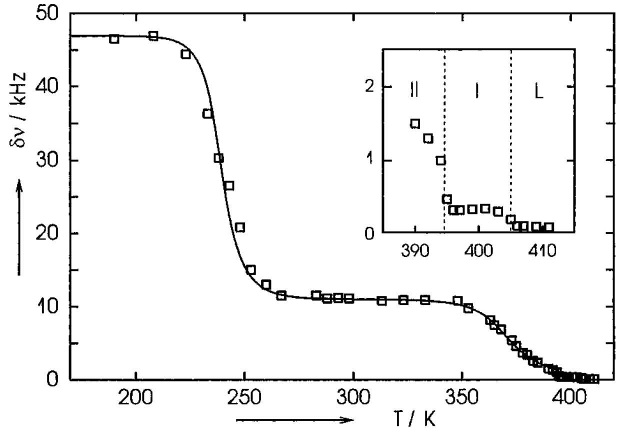


Figure 5. Proton line width (full width at half maximum height) of the *sym*-cubane-d_2 sample vs the absolute temperature, recorded at 300 MHz. The insert shows details in the temperature range of the solid II → solid I and solid I → liquid transitions. The symbols are experimental points, while the full line is calculated as explained in the text.

interactions and must therefore correspond to self-diffusion of the cubane molecules between the lattice sites. At the solid II → solid I transition a discontinuous reduction of the line width occurs down to 300 Hz, indicating that the self-diffusion is considerably faster in solid I. Another small discontinuous reduction in the line width to less than 100 Hz occurs on melting to the liquid phase. In this phase the line width is dominated by sample and field inhomogeneity effects.

An exact quantitative analysis of the proton line width is not possible, but a good estimate of the correlation times involved in the two processes can be obtained by analyzing the results in terms of the equation[13]

$$\delta\nu^2 = \delta\nu_1^2\frac{2}{\pi}\tan^{-1}(2\pi\alpha_1\delta\nu\tau) + \delta\nu_2^2\frac{2}{\pi}\tan^{-1}(2\pi\alpha_2\delta\nu\tau_\mathrm{d}) \qquad (4)$$

Here we assume that the square of the observed line width consists of two contributions. The first, $\delta\nu_1^2$, corresponds to the intramolecular dipolar interactions, which are averaged out by the cubic jumps, characterized by the correlation time τ. The second, $\delta\nu_2^2$, corresponds to the intermolecular interactions between the rapidly reorienting molecules in their lattice sites. This part is averaged out by the self-diffusion process, characterized by the correlation time τ_d. The first (low temperature) plateau in Figure 5 thus corresponds to $(\delta\nu_1^2 + \delta\nu_2^2)^{1/2}$, and the second to $\delta\nu_2$. The parameters α_1 and α_2 are numerical factors of order unity which are, following Abragam,[13] rather ill-defined.

To analyze the results of Figure 5 in terms of eq 4, we first fitted the low temperature data with the rate equation for the reorientation process, eq 3, obtaining $\alpha_1 = 0.13$ (which illustrates Abragam's qualification "ill-defined"), $\delta\nu_1^2 = 21 \times 10^8$ s^{-2} and $\delta\nu_2^2 = 1.2 \times 10^8$ s^{-2}. The high temperature data were then used to calculate τ_d (assuming $\alpha_2 = 1$). The results are plotted in Figure 3 with the symbol △ and yield the Arrhenius equation

$$\tau_\mathrm{d} = \tau_\mathrm{d}^0 \exp(E_\mathrm{d}/RT) \qquad (5)$$

with $E_\mathrm{d} = 83$ kJ mol^{-1} and $\tau_\mathrm{d}^0 = 2.5 \times 10^{-17}$ s. The value of τ_d^0 is at best a rough estimate since the uncertainty of α_2 fully translates into the uncertainty of τ_d^0. Applying Einstein's relation for the self-diffusion coefficient

$$D = \frac{r^2}{6\tau_\mathrm{d}}\frac{1}{} \qquad (6)$$

and identifying the jump distance r with the lattice constant a yields

$$D = D^0 \exp(-E_\mathrm{d}/RT) \qquad (7)$$

where $D^0 = 1.9 \times 10^{-3}$ m^2 s^{-1}. This result is well within the range of values found in other orientationally disordered compounds of cagelike molecules, similar in size to cubane.[16] Again, we do not have sufficient data in the solid I phase for a similar analysis to be made. However, from the observed line width an estimated value of $D = 8 \times 10^{-14}$ m^2 s^{-1} in the midpoint of this phase may be calculated.

For completion, we have also measured the T_1 of the protons in the cubane-d_2 sample. The results, shown in Figure 6, exhibit a very similar behavior to that shown in Figure 4 for deuterium. There is a clear T_1 minimum and two discontinuities at the solid II → solid I and solid I → liquid transitions. The proton T_1 results are, however, more difficult to interpret quantitatively because they are affected by many dipolar interactions of similar magnitude. We may, nevertheless, attempt to fit the data with the BPP type equation

$$\frac{1}{T_1} = K^2\left[\frac{\tau}{1 + \omega_0^2\tau^2} + \frac{4\tau}{1 + 4\omega_0^2\tau^2}\right] \qquad (8)$$

where K should be of the order of the dipolar field, expressed in angular frequency units, experienced by a proton due to its nearest neighboring protons. Its (experimental) value, as calculated from the T_1 minimum (0.54 s), is $K = 4.95 \times 10^4$ s^{-1}. This may be compared with the intramolecular contribution to the rigid-lattice second moment of the proton resonance line (powder average)[13]

$$\langle\Delta\omega^2\rangle = \frac{3}{5}\gamma_\mathrm{H}^4\hbar^2 I(I+1)\sum_k \frac{1}{r_\mathrm{jk}^6} \qquad (9)$$

where j indicates an arbitrary proton in the cubane molecule and the summation is over all other protons in the same molecule. The calculated value of $\langle\Delta\omega^2\rangle^{1/2}$, which is 3.83×10^4 s^{-1}, perfectly supports our interpretation of K. From the measured temperature dependence of T_1 and the experimental result for K, the τ values in eq 8 were determined. They are plotted in Figure 3 with the symbol +. In general they are consistent with those obtained from the deuterium spectra, although at around room temperature and below they deviate somewhat, apparently due to the presence of another relaxation process.

The Deuterium NMR Spectrum in Solid I and in the High Temperature Region of Solid II. Up to now, the discussion of the deuterium spectra of cubane-d_2 has implied that in the fast exchange regime the spectrum can be described by a single Lorentzian line. The width of this line should gradually narrow with increasing temperature. This behavior is in fact observed up to about 340 K, where the line width is around 0.4 kHz. However, above this temperature the spectrum exhibits features which gradually evolve into a Pake doublet corresponding to a very small, axially symmetric quadrupole coupling tensor with $Q'_\mathrm{c} = 0.48$ kHz. The structure persists on transition to solid I, but disappears on melting. Examples of spectra in both phases are shown in Figure 7. The spectra are not always reproducible and continuously change with time during the measurements.

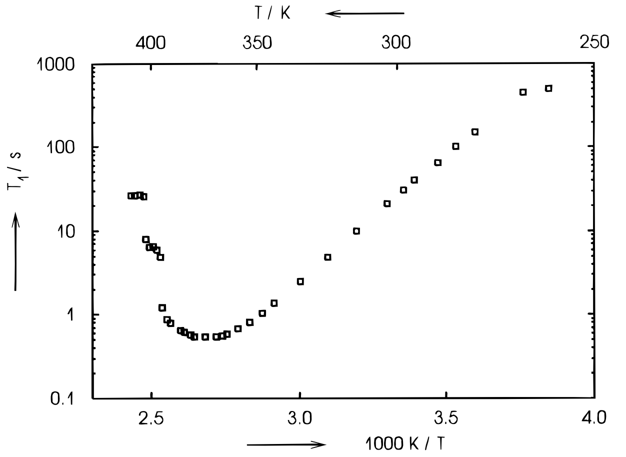


Figure 6. Proton T_1 results of the *sym*-cubane-d_2 sample at 300 MHz vs the reciprocal absolute temperature.

They are sometimes not symmetric and often exhibit sharp features. We believe that this behavior arises from continuous sublimation of the cubane within the sample tube, even during the measurements, and the formation of a coarse-grained texture. There can, however, be no doubt that the deuterons experience a finite residual quadrupole coupling interaction (less than 0.3% of the static value) and that, therefore, the averaging process due to reorientations cannot be strictly cubic. To check whether this interaction could already exist at lower temperatures, we have simulated Pake doublets with varying ratios of the line width to Q'_{c}. These simulations convinced us that such a Pake doublet would not be detected in the experimental spectra recorded below 340 K. We therefore conclude that the small deviation from perfect cubic jumps most likely exists over the entire dynamic range, but it becomes observable only at higher temperatures when the homogeneous lines become sufficiently narrow.

The small deviation from cubic symmetry has probably a negligible effect on the quantitative kinetic analysis given in the previous sections; however, its origin is intriguing. In the solid II phase with space group $R\bar{3}$ it could arise from an isotope effect on the orientation of the *sym*-cubane-d_2 D−D axis, or from differences in the static Q_{c} values for different orientations of the D−D axis in the crystal. In this phase there is a unique axis with S_6 symmetry, and one of the main diagonals of the cubane molecule is aligned along this direction. If the probability of the D−D axis to align along S_6 is not exactly the same as for the other (H−H) main diagonals, the statistical average of the deuterium quadrupole coupling interaction over all the cubic orientations will not be zero. Likewise, if the value of Q_{c}, when the D−D axis is along S_6, is not identical to that when the molecule aligns along the other directions, the average quadrupole coupling interaction will not vanish exactly either. We cannot tell from the experimental results which of the two effects is responsible for the deviation from exact cubic symmetry, nor whether both are present. The effect itself, however, is not inconsistent with the symmetry of solid II and the *sym*-cubane-d_2 molecule. It is nevertheless a remarkable effect and we are not aware of any similar case in other molecular crystals.

The situation is more complicated for solid I. Although the structure of this phase has not yet been determined, it most probably belongs to one of the cubic space groups. This conjecture is based on the assumption that the endothermic transition of solid II to solid I is associated with a structural change and that, as is usual, this change is to a more symmetric phase. Since $\mathrm{R}\bar{3}$ has only cubic supergroups we anticipate that solid I is cubic. In fact the rhomboedric unit cell of solid II with $\alpha = 72.26°$ is already very close to cubic (for $\alpha = 70.53°$ it *would* be cubic). If solid I is indeed cubic, the explanation offered for $Q'_{\mathrm{c}} \neq 0$ in solid II cannot apply to this phase: In a cubic structure there is no unique direction, and an isotope effect on the alignment of the D−D axis cannot be invoked.

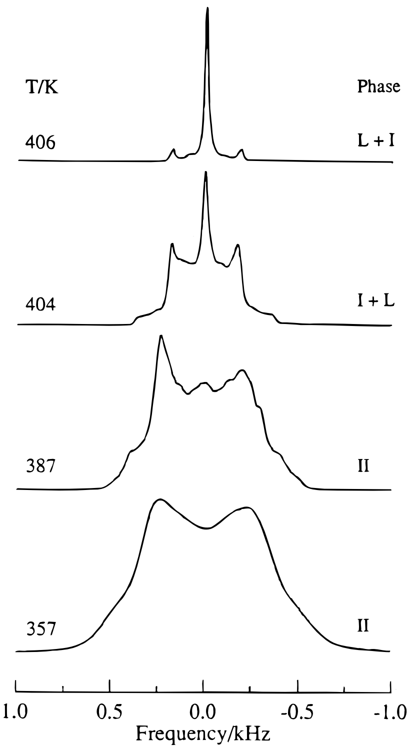


Figure 7. Deuterium NMR spectra in solid I and in the high temperature region of solid II. The central line in the 406 K and 404 K spectra arises from the liquid (L) coexisting with solid I at these temperatures. Note the highly expanded scale compared to the spectra in Figure 2.

A possible explanation for $Q'_{\mathrm{c}} \neq 0$ in solid I could involve a cooperative alignment of the D−D axes. If the orientation of this axis in one molecule depends on the orientation of the D−D axis in a neighboring one, causing both to preferentially align in parallel, domains will be formed with spontaneous polarization of the D−D axes in a lattice that is otherwise cubic. If, in addition, the lifetime of these (hypothetical) domains is sufficiently long, a residual quadrupole interaction, as we have observed it, will survive. We are currently attempting to determine the structure of solid I by powder X-ray diffraction. Hopefully the method will prove sensitive enough to distinguish between the $R\bar{3}$ structure of solid II and that of solid I. On a more optimistic level, if the latter turns out to be cubic we may even hope to find structural differences between normal cubane and *sym*-cubane-d_2.

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References and Notes

(1) The other two are tetrahedrane and dodecahedrane. The analogues of the icosahedron and octahedron are not accessible to synthesis, at least not from a carbon skeleton.

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