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Orientational order and dynamics of molecules in the nematic phase 4-trans-(4-trans-n-propylcyclohexyl)cyclohexanenitrile

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Orientational order and dynamics of molecules in the nematic phase of 4-*trans*-(4-*trans*-*n*-propylcyclohexyl)cyclohexanenitrile

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A sample of 4-*trans*-(4-*trans*-*n*-propylcyclohexyl)cyclohexanenitrile (CCH3) has been synthesized containing six deuterons randomly distributed between axial and equatorial positions in the cyanylated ring. The local orientational order parameters for axes fixed in this ring have been measured by obtaining the deuterium N.M.R. spectrum. The results show that the lack of symmetry and flexibility of the molecule affect the order matrix. The biaxiality in the local order matrix is small and could be close to zero, depending on the location, as yet unknown, of the principal axes. The spectral densities $J_1(\omega)$ and $J_2(\omega)$ have been measured for a sample oriented with the director orthogonal to B_0. It is shown that these spectral densities cannot be explained by the mechanism of relaxation being caused solely by director fluctuations. It is also not possible to explain the spectral densities by invoking only small-step rotational diffusion. A combination of these two relaxation mechanisms does fit the data.

1. Introduction

Most thermotropic liquid crystals contain an aromatic fragment, often referred to as the core, which is meant to imply the dominant role played by interactions between this group and other molecules in determining the liquid-crystalline properties. This domination of the intermolecular potential was often thought to stem from the large anisotropic electric polarizability of the π-electron system, and it was surprising therefore when it was discovered [1] that replacing aromatic rings by relatively unpolarizable cyclohexane groups gives molecules with almost equivalent liquid-crystal-forming propensity. It would clearly be interesting to compare the behaviour of molecules in related aromatic and aliphatic mesogens, and this is the motivation behind our study of CCH3, whose structure and transition temperatures are shown in figure 1. This molecule is the first in the homologous series to show a stable liquid-crystalline phase, and as such it is compared with the first member of the 4-*n*-alkyl-4′-cyanobiphenyl series, that with $n = 5$ (5CB) in figure 1. T_{NI} and $T_{NI}-T_C$, where T_C is the melting point, are both greater for CCH3 than for 5CB, which is one indication that the saturated-ring compound is a ‘better’ liquid crystal; that is, the anisotropic interactions between molecules are stronger.

In order to gain greater insight into the molecular behaviour of CCH3, we have attempted to measure the orientational order of the molecules. This is a difficult task for a flexible molecule and is best approached by using deuterium N.M.R. [2]. The quadrupolar splitting $\Delta\tilde{\nu}_i$ for a deuteron at the ith site is, to a good approximation, directly proportional to S^i_{CD}, the order parameter for the C–D bond at this site. If we assume that CCH3 exists in a finite set of conformational states then measuring $\Delta\tilde{\nu}_i$

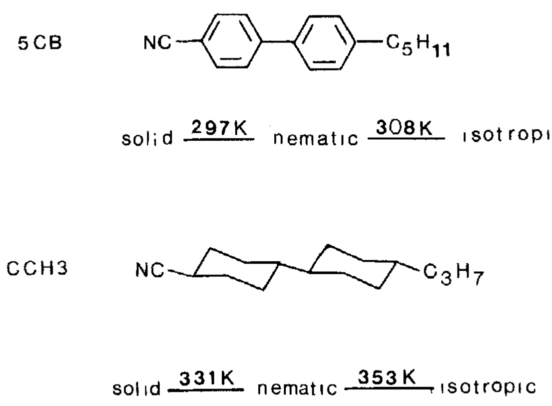

Figure 1. Structure and phase behaviour of CCH3 and 5CB.

for deuterons in each rigid sub-unit of the molecule enables models of the potential of mean torque to be tested.

However, it proved difficult to obtain a CCH3 molecule labelled with deuterium in each rigid sub-unit, and hence we present here a preliminary study of ordering by monitoring the quadrupolar splittings of deuterons at each site in the cyanylated ring.

The orientational order parameters are ensemble averages and are a description of the system at equilibrium. They do not reveal how the molecules move in the liquid-crystalline phase, and hence give an incomplete picture of molecular behaviour. The dynamics of the molecules can be studied via N.M.R. relaxation times, and here too there is an advantage in studying the deuteron [3]. Relaxation experiments have been developed that enable separate spectral densities $J_m(\omega)$ to be obtained for deuterons in oriented samples, and we shall describe such measurements for the deuterons in our sample of CCH3. Our sample is only partially deuteriated and hence can give only partial information on the dynamics. There are, however, two sets of differently oriented C–D bonds in the deuteriated ring, those at equatorial or axial positions, and hence four spectral densities are obtained with which to test models for the motions responsible for spin relaxation.

2. Experimental

The synthesis of CCH3-d_6 started from 4-(4-*trans*-*n*-propylcyclohexyl)benzoic acid, which was supplied by E. Merck (Darmstadt). This was converted to the methyl ester by refluxing 10 g with 0·5 ml of concentrated sulphuric acid and 110 ml of methanol for four hours. The solution was poured into water and extracted with carbon tetrachloride (2 × 50 ml) and the combined extracts were dried over magnesium sulphate. Evaporation of the solvent left a yellowish solid, which was recrystallized from methanol to give the methyl ester in 85 per cent yield, m.p. 38·5–39·5°C. The benzene ring was reduced to a cyclohexane ring by reacting the methyl ester (2 g) dissolved in acetic acid-d_1 (10 ml) with platinum dioxide (40 mg) and deuterium gas (6 atm). This mixture was stirred for 24 h at ambient temperature, filtered through calcite and evaporated to give an oily residue, which crystallized on standing. Recrystallization from pentane gave deuteriated methyl-4-(4-*n*-propylcyclohexyl)-cyclohexane carboxylate in 96 per cent yield, m.p. 56–61°C. The proton N.M.R. spectrum confirmed that the cyclohexane ring substituted with the $COOCH_3$ group contained six deuterons, and also the presence of two methyl resonances in the ratio 4 : 1 showed that the product of reduction was a mixture of the *trans*, *cis* and *trans*, *trans* isomers. By analogy with the reduction of related benzoate esters [4], it was assumed that *trans*, *cis* was the major product. Attempts to change the equilibrium in favour of the *trans*, *trans* isomer by the method described by Fieser and Leffler [4] were only partially successful. The isolation of the *trans*, *trans* acid was achieved by the staff of the laboratories of E. Merck (Darmstadt). The next stage in the synthesis was the conversion of the acid (2·58 g) to the acid chloride by refluxing for two hours with a small excess of thionyl chloride (10 g). Excess thionyl chloride was distilled off, leaving the acid chloride as a colourless oil.

The crude acid chloride was added dropwise to concentrated ammonia solution (50 ml) and the precipitate filtered, using the filtrate to wash out the flask. The solid was air-dried on filter paper to give the amide in 91 per cent yield, m.p. 236·8°C. The final step was to convert the amide to the nitrile. The amide (1 g) was refluxed in phosphoryl chloride (15 g) for one hour, and then the excess phosphoryl chloride was distilled off, and on cooling the residue was treated with deuterium oxide (5 g). The slurry was neutralized by careful addition of solid sodium carbonate and the mixture extracted with ether (3 × 20 ml). The combined extracts were washed with water (50 ml), dried over magnesium sulphate and evaporated to give a pale yellow oil, which crystallized on standing. The solid was purified by chromatography on alumina using light petroleum as eluent, and then recrystallized from pentane to constant melting point. The nitrile was obtained as colourless needles in 87 per cent yield, m.p. 57–58°C (lit. 58°C).

The deuteron N.M.R. spectra were recorded at 30·7 MHz on a Bruker CXP 200 spectrometer, and a typical spectrum is shown in figure 2. There are six deuterons in axial positions and four in equatorial, and the spectrum shows that these form two separate essentially equivalent groups. The Zeeman spin–lattice relaxation rate R_{1Z} and the rate of loss of quadrupolar order R_{1Q} were obtained simultaneously from the Jeener–Broekaert experiment:

$$90^\circ_x–\tau–45^\circ_y–t_d–45^\circ_x–t_R–45^\circ_{-x}–t_R–$$

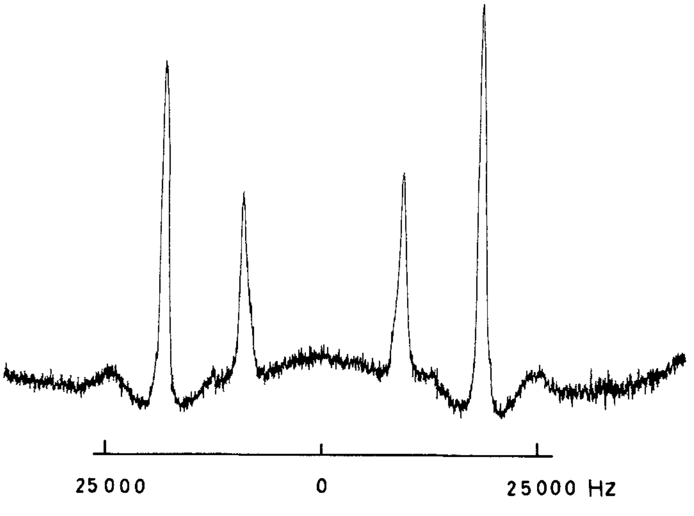

Figure 2. 30·7 MHz spectra of deuterons in CCH3-d_6.

with appropriate phase cycling [3]. The sample was contained in a 5 mm o.d. sample tube and the probe had a 5 mm diameter solenoid coil, which gave a 90° pulse width of 2.4 μs. The delay τ was adjusted to be $(2\Delta\tilde{v}_i)^{-1}$, where $\Delta\tilde{v}_i$ is the quadrupolar splitting for axial or equatorial deuterons. About 15 relaxation delays were used, and t_R, the time necessary for recovery of equilibrium, was greater than $5T_1$. Inclusion of the 45°_{-x} pulse in the sequence gives a signal that is directly proportional to the difference magnetisation $M(t_d) - M(\infty)$.

3. Results and discussion

3.1. *Orientational order*

We note first that it is often assumed that the orientational order in liquid crystals can be described by a single order parameter $\bar{P}_2$. In this case the ratios of pairs of second-rank tensor components along the director, $\tilde{A}_\parallel$, are independent of $\bar{P}_2$ and hence of temperature. The use of a single order parameter is valid if the molecules are rigid and cylindrically symmetric; neither of these conditions, however, hold for CCH3. In this case the ratios $\Delta\tilde{v}_a/\Delta\tilde{v}_e$ could change with temperature, the exact magnitude of the effect depending on the departure from cylindrical symmetry of the ordering potential and the conformational distribution. In figure 3 we show the temperature dependence of $\Delta\tilde{v}_a/\Delta\tilde{v}_e$, and there is indeed a decrease in this ratio as temperature decreases. In principal, therefore, a single independent order parameter is insufficient to describe the ordering of CCH3.

The change produced in $\Delta\tilde{v}_a/\Delta\tilde{v}_e$ is of the order of 5 per cent, and to relate this to the separate effects of molecular biaxiality and flexibility is not possible from our data. We can, however, calculate local order parameters S_{zz} and $S_{xx} - S_{yy}$ for the deuteriated ring from $\Delta\tilde{v}_a$ and $\Delta\tilde{v}_e$. The anisotropy of the molecular diamagnetic susceptibility of CCH3 is negative, which means that the mesophase directors are aligned orthogonally to the applied magnetic field. In this case $\Delta\tilde{v}_a$ and $\Delta\tilde{v}_e$ are given by [2]

$$\begin{aligned}\Delta\tilde{v}_i = {} & -\tfrac{3}{8}q_{ibb}\,\{S_{zz}[(3l^2_{zbi} - 1) + \eta_i\,(l^2_{azi} - l^2_{czi})] \\ & + (S_{xx} - S_{yy})\,[(3l^2_{xbi} - 3l^2_{ybi}) + \eta_i(l^2_{axi} - l^2_{cxi} - l^2_{ayi} + l^2_{cyi})]\}. \qquad (1)\end{aligned}$$

The direction cosines l_{azi} etc. relate the principal axes (xyz) of $\mathbf{S}$ to the principal axes (abc) of the quadrupole interaction tensor $\mathbf{q}_i$ at the ith site. The asymmetry parameter

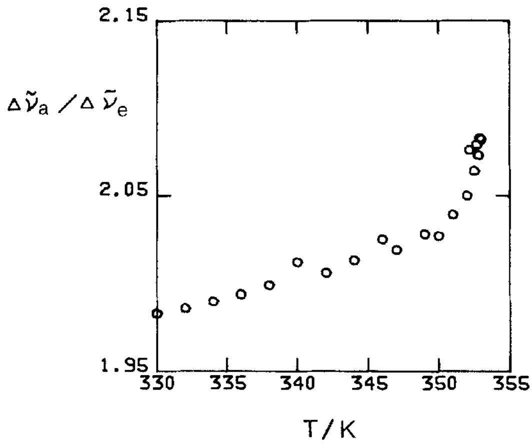

Figure 3. Ratio of $\Delta\tilde{v}_a/\Delta\tilde{v}_e$ quadrupolar splittings of axial and equatorial deuterons as a function of temperature.

η_i is defined as $(q_{iaa} - q_{icc})/q_{ibb}$ with a and c chosen so that η is positive. The b axis can be located with high precision to lie along the C–D bond direction, and η for deuterons in aliphatic compounds is close to zero.

The spectra of CCH3-d_6 yield two quadrupolar splittings, and hence values of S_{zz} and $S_{xx} - S_{yy}$ can be obtained only by assuming the orientation of the xyz axes; one of these axes by symmetry lies parallel to the C_2C_6 direction, and if one extra second-rank quantity could be measured for nuclei in the ring, such as the dipolar coupling, then the precise orientation of the axes would be known. For a disubstituted cyclohexane ring with the same substituent at equatorial positions on carbons 1 and 4, the remaining two principal axes can be identified as the C–D (axial) bond direction (x), and z as orthogonal to x and y. We shall therefore explore the consequences, in terms of the magnitudes of the principal elements of S, of adopting these axes for CCH3. We also assume an undistorted tetrahedral geometry at each carbon atom, which served to fix the direction cosines in equation (1). It remains to choose values for q_{ibb} and η_i; the asymmetry parameter when it has been measured [5], is found to be $< 0{\cdot}1$ for most deuterons, so we shall at first set it to zero. The quadrupole coupling constant is insensitive to substitution, and we shall assume equal values for axial and equatorial sites, and we use 170 kHz as a typical value for aliphatic deuterons [6]. The signs of $\Delta\tilde{\nu}_a$ and $\Delta\tilde{\nu}_e$ are not apparent from the N.M.R. spectrum, but they can be determined by assuming the signs of S_{zz} and S_{xx}. Thus for a rod-like molecule we expect the longer axis z to be ordered preferentially parallel to one another, so that S_{zz} should be positive. The ordering matrix approximates to cylindrical symmetry, so that $S_{yy} \approx -\frac{1}{2} S_{zz}$, and hence should be negative. The values of S_{zz} and $S_{xx} - S_{xx}$ obtained with these assumptions are shown in figure 4.

The temperature dependence of S_{zz} is not unusual, and it is interesting to note the value at T_{NI} of $0{\cdot}404 \pm 0{\cdot}005$, which is considerably greater than $S_{zz}^{NI} = 0{\cdot}338 \pm 0{\cdot}001$

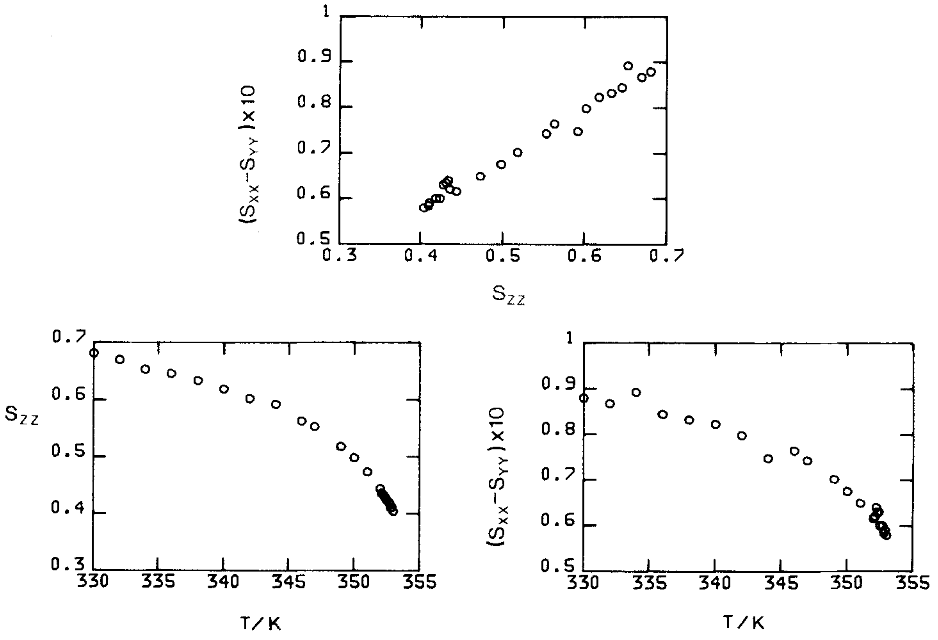

Figure 4. Temperature dependences of S_{zz} and $S_{xx} - S_{yy}$, the local order parameters for the deuteriated ring in CCH3-d_6.

for the aromatic rings of 5CB [6], and is close to the value of 0·429 predicted for a rigid axially symmetric mesogen that obeys the Maier–Saupe form for the potential of mean torque [7]. The temperature dependence of $S_{xx} - S_{yy}$ is unusual: the biaxiality in **S** for a rigid body reaches a maximum close to $S_{zz} = 0{\cdot}4$ [8], whereas for CCH3 there is no evidence that a maximum in $S_{xx} - S_{yy}$ is being approached, even for $S_{zz} > 0{\cdot}6$. This behaviour might be a consequence of the flexibility of CCH3, although for 5CB the biaxiality in ordering of the aromatic group does not show this unusual behaviour. It could also be a result of our assumptions about the location of the principal axes of **S**, or our choice of a zero value for η. The effect of a finite η is difficult to test because neither its magnitude nor the location of the principal axes a and c of **q** are known. Choosing a to lie in the CD$_2$ plane for each deuteron and varying η from $+0{\cdot}06$ to $-0{\cdot}06$ has only a small effect on the order parameters, and does not change the nature of the temperature dependence of $S_{xx} - S_{yy}$. A positive value of η decreases both S_{zz} and $S_{xx} - S_{yy}$ by approximately 5 per cent and 20 per cent respectively, whereas a negative η increases these two order parameters in each case by similar amounts. Rotating the principal axes of **S** about y either increases or decreases $S_{xx} - S_{yy}$, depending on the direction of rotation, and a value for $\beta_{\mathrm{CD}z}$ of 76° for axial deuterons brings $S_{xx} - S_{yy}$ close to zero for all temperatures when $\eta = 0{\cdot}06$.

3.2. *Relaxation and molecular dynamics*

The Jeener–Broekaert experiment on a sample with the director parallel to the magnetic field gives the two spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$, which are defined here as

$$J_{m_L}(\omega) = \int_0^\infty \overline{F_Q^{(2,m_L)}(0)F_Q^{(2,m_L)*}(t)} \cos m_L\omega t \, dt. \tag{2}$$

$F^{(2,m_L)}$ is a component of the irreducible tensor representing the deuteron quadrupolar interaction and refers to axes fixed with z along the magnetic field. Note that these spectral densities include the strength of the quadrupolar interaction, and hence they differ from those that do not [3, 9] by a factor $\frac{3}{2}\pi^2 q_{ibb}^2$. When the director is at an angle β_{nB} to $\mathbf{B}_0$ the spectral densities measured experimentally, $J_{m_L}(m_L\omega_0, \beta_{nB})$, are [10]

$$J_{m_L}(m_L\omega_0, \beta_{nB}) = \sum_{m_D} [d^2_{m_D m_L}(\beta_{nB})]^2 \, J_{m_D}(m_L\omega_0), \tag{3}$$

where $m_D = 0, \pm 1, \pm 2$, and $J_m(\omega) = J_{-m}(\omega)$; $d^2_{m_D m_L}(\beta_{nB})$ is a reduced Wigner function [11], and ω_0 the Larmor frequency. When **n** and $\mathbf{B}_0$ are orthogonal

$$J_1(\omega_0\, 90°) = \tfrac{1}{2}J_1(\omega_0) + \tfrac{1}{2}J_2(\omega_0) \tag{4}$$

and

$$J_2(2\omega_0\, 90°) = \tfrac{3}{8}J_0(2\omega_0) + \tfrac{1}{2}J_1(2\omega_0) + \tfrac{1}{8}J_2(\omega_0). \tag{5}$$

The spectral densities $J_m(\omega)$ depend upon the strength of the quadrupole interaction and, more interestingly, on the nature of the motion of the molecules. In order to interpret the experimentally determined rates, it is therefore necessary to decide which motional modes affect the relaxation rates. These are of three kinds: motion of the whole molecule, internal modes of motion, and collective modes of motion that give rise to fluctuations in the director. These latter modes of motion are unusual in that they contribute only to $J_1(\omega)$, provided that they are small in amplitude. For a rigid axially symmetric molecule the contribution made to $J_1(\omega)$ by director fluctuations can be written as [12],

$$\begin{aligned} J_1^{\mathrm{DF}}(\omega) &= A\bar{P}_2^2\,[P_2(\cos\beta_{\mathrm{CD}})]^2\omega^{-1/2}, \\ &= A_{\mathrm{DF}}\,[P_2(\cos\beta_{\mathrm{CD}})]^2, \end{aligned} \qquad (6)$$

where we have assumed that these slow collective modes are not strongly coupled to the motion of the whole molecule. The angle β_{CD} is that between the C–D bond of interest and the symmetry axis, and $\bar{P}_2$ is the order parameter for this axis. The constant A depends on the elastic constants and viscosity coefficients of the sample. If we assume that CCH3 is essentially rigid and axially symmetric and that relaxation is dominated by this term then the ratio $J_1^{\mathrm{ax}}(\omega_0\ 90°)/J_1^{\mathrm{eq}}(\omega_0\ 90°) = R_1$ should be $[P_2(\cos\beta_{\mathrm{ax}})/P_2(\cos\beta_{\mathrm{eq}})]^2$. This ratio depends upon where we locate the assumed symmetry axis for CCH3. If we take this to be the choice that minimizes $S_{xx} - S_{yy}$ then $\beta_{\mathrm{ax}} = 76°$ and $\beta_{\mathrm{eq}} = 62{\cdot}8°$, so that the ratio is 4·9. If we assume z to be orthogonal to the axial bonds then $\beta_{\mathrm{ax}} = 90°$ and $\beta_{\mathrm{eq}} = 61{\cdot}8°$, so that $R_1 = 9$. The experimental ratio varies between 2·0 close to T_{NI} to 1·6 at 303 K ($T_{\mathrm{NI}} - T = 48$ K), and it is therefore clear that director fluctuations alone cannot account for the observed spectral densities. This conclusion is reinforced by noting that the ratio $J_1(\omega_0, 90°)/J_2(\omega_0, 90°)$ should be $\sqrt{2}$, independently of the site of the deuteron, if director fluctuations dominate the spectral densities. The observed values are temperature-dependent for both axial and equatorial deuterons and have the values of 1·20 (axial) and 1·06 (equatorial) at T_{NI}, and 1·52 and 1·26 respectively at $T_{\mathrm{NI}} - T = 48$ K.

These observations eliminate the possibility that director fluctuations alone dominate the magnitudes of $J_{m_L}(m_L\omega_0, 90°)$, and hence the effect of molecular rotations must be important. Our data cannot be used to asses the relative importance of whole-molecule and internal modes of motion, because the deuterons we have studied are located within one rigid sub-unit of the molecule. We shall therefore assume, that the molecule is rigid, in which case the correlation function in equation (2) is obtained by expressing the tensor components $F_Q^{(2,m_L)}$ as

$$F_Q^{(2,m_L)} = \sum_{m_M} D^2_{m_M,m_L}(\Omega_{LM})F_Q^{(2,m_M)}, \qquad (7)$$

where the $F_Q^{(2,m_M)}$ are components of the same tensor in a frame fixed in the molecule, and $D^2_{m_M,m_L}(\Omega_{LM})$ is the Wigner rotation matrix that relates this frame to that fixed by the magnetic field direction. The values of m_M are ± 2, ± 1, 0, and assuming the molecule to be cylindrically symmetric restricts m_M and m'_M to be equal. The time dependence now lies entirely in the Wigner rotation matrices; thus

$$\overline{F_Q^{(2,m_L)}(0)F_Q^{(2,m_L)}(t)^*} = \sum_{m_M} \overline{D^2_{m_M m_L}(\Omega_{LM}(0))D^2_{m_M m_L}(\Omega_{LM}(t)^*)}\; F_Q^{(2,m_M)}F_Q^{(2,m_M)*}. \qquad (8)$$

Finally, we relate the $F_Q^{(2,m_M)}$ to components in the principal frame of the deuterium quadrupolar tensor, and this involves the time-independent transformation

$$F_Q^{(2,m_M)} = \sum_{m_Q} F_Q^{(2,m_Q)}D^2_{m_Q m_M}(\Omega_{QM}). \qquad (9)$$

The quadrupolar tensor in the principal frame has non-zero components for $m_Q = \pm 2, 0$, and in practice the biaxial components $F_Q^{(2,\pm 2)}$ are small and can be neglected when calculating relaxation rates, so that only the term with $m_Q = 0$ in equation (9) is retained. This gives

$$\overline{F_Q^{(2,m_L)}(0)F_Q^{(2,m_L)}(t)^*} = \tfrac{3}{2}\pi^2 q_{bb}^2 \sum_{m_M} \overline{D^2_{m_M m_L}(\Omega_{LM}(0))D^2_{m_M m_L}(\Omega_{LM}(t)^*)}\, |D^2_{0m_M}(\Omega_{QM})|^2. \quad (10)$$

We shall start by adopting the small-step rotational-diffusion model for the motion of the molecules, so that

$$\overline{D^2_{m_M m_L}(\Omega_{LM}(0))D^2_{m_M m_L}(\Omega_{LM}(t)^*)} = \overline{|D^2_{m_M m_L}|^2} \exp\left(\frac{-t}{\tau^{(2)}_{m_M m_L}}\right), \quad (11)$$

where

$$(\tau^{(2)}_{m_M m_L})^{-1} = \frac{D_\perp}{\beta^{(2)}_{m_M m_L}} + m_M^2(D_\parallel - D_\perp). \quad (12)$$

The rotational-diffusion constants $D_\parallel$ and $D_\perp$ refer to directions parallel and perpendicular to the assumed symmetry axis of the molecule, which we identify as the molecular z axis. The term $\beta^{(2)}_{m_M m_L}$ depends on the potential of mean torque for the molecules in the nematic phase, and values of this quantity are given by Agostini *et al.* [13] for a Maier–Saupe potential of mean torque. The $\beta^{(2)}_{m_M m_L}$ depend upon values of $\bar{P}_2$, the order parameter for the z axis, which is identical with S_{zz}. The averages $\overline{|D^2_{m_M m_L}|^2}$ depend on S_{zz}, but also on $\bar{P}_4$, and this fourth-rank order parameter is calculated with the Maier–Saupe potential.

Substituting equations (10) and (11) into (2) gives the spectral densities at the *i*th site (*i* denoting axial or equatorial deuterons) as

$$J^{\mathrm{R},i}_{m_L}(m_L\omega_0) = \tfrac{3}{2}\pi^2 q_{ibb}^2 \left\{ \frac{\overline{|D^2_{m_L 0}|^2}\,[d^2_{00}(\beta_i)]^2 \tau^{(2)}_{m_L 0}}{1 + (m_L\omega_0\tau^{(2)}_{m_L 0})^2} + \frac{2\overline{|D^2_{m_L 1}|^2}\,[d^2_{01}(\beta_i)]^2 \tau^{(2)}_{m_L 1}}{1 + (m_L\omega_0\tau^{(2)}_{m_L 1})^2} \right.$$
$$\left. + \frac{2\overline{|D^2_{m_L 2}|^2}\,[d^2_{02}(\beta_i)]^2 \tau^{(2)}_{m_L 2}}{1 + (m_L\omega_0\tau^{(2)}_{m_L 2})^2} \right\}, \quad (13)$$

where β_i is the angle that the *i*th C–D bond makes with the z axis. The superscript R signifies that only molecular rotation contributes to these spectral densities.

Equations (13), (4) and (5) can be combined to obtain calculated values of $J^{\mathrm{R},i}_{m_L}(m_L\omega_0, 90°)$, which can be brought into optimum agreement with the four observed spectral densities by varying $D_\parallel$, $D_\perp$ and the reduced Wigner functions $d^2_{0m}(\beta_i)$. The angular functions are determined by the geometry of the cyclohexane fragment containing the deuterons, and the location of the axis of assumed cylindrical symmetry for the rotational-diffusion tensor. The geometry of the ring is assumed to be that adopted when determining elements of the ordering matrix, that is with tetrahedral dispositions of the bonds at each carbon atom. Small variations from this geometry are of course possible, but these do not have a large effect on the calculated spectral densities. The location of the symmetry axis for the diffusion tensor does have a large effect on the predicted values of $J^{\mathrm{R},i}_{m_L}(m_L\omega_0)$. We expect this axis to coincide approximately with that for which the ordering matrix is cylindrically symmetric. However, it was found that the calculated values of $J^{\mathrm{R},i}_{m_L}(m_L\omega_0)$ cannot be brought into agreement with the experimental values of $J^{\mathrm{eq}}_1(\omega_0, 90°)$, $J^{\mathrm{eq}}_2(\omega_0, 90°)$, $J^{\mathrm{ax}}_1(\omega_0, 90°)$ and $J^{\mathrm{ax}}_2(2\omega_0, 90°)$ for any choice of the location of the symmetry axis.

This failure to reach agreement between the experimental spectral densities and those predicted taking into account only the rotational motion of the whole molecule may be a consequence of the approximations inherent to this molecule, but it may also be a consequence of neglecting the contribution to the spectral densities from director fluctuations. We have therefore explored a model in which both $J_{m_L}^{\mathrm{R},i}(m_L\omega_0)$ and $J_1^{\mathrm{DF},i}(\omega_0)$ contribute to the values of $J_{m_L}^i(m_L\omega_0, 90°)$, so that

$$J_1^i(\omega_0, 90°) = \tfrac{1}{2}[J_1^{\mathrm{R},i}(\omega_0) + J_2^{\mathrm{R},i}(\omega_0) + J_1^{\mathrm{DF}}(\omega_0)] \tag{14}$$

and

$$J_2^i(2\omega_0, 90°) = \tfrac{3}{8}J_0^{\mathrm{R},i}(2\omega_0) + \tfrac{1}{2}J_1^{\mathrm{R},i}(2\omega_0) + \tfrac{1}{8}J_2^{\mathrm{R},i}(2\omega_0) + \tfrac{1}{2}J_1^{\mathrm{DF},i}(2\omega_0) \tag{15}$$

The variable parameters now include A, the constant in equation (6), and in this case a good fit is obtained between calculated and observed spectral densities when the symmetry axis for diffusional motion coincides with the z axis, which gives an axially symmetric ordering matrix, as shown by the data in figure 5. The temperature dependences of $D_\parallel$ and $D_\perp$ are shown in figure 6, and that of $D_\parallel$ fits an Arrhenius-type behaviour within experimental error, giving an activation energy $E_\parallel^{\mathrm{a}}$ for rotation about the symmetry axis z of 43·07 kJ mol^{-1}. The temperature dependence of $D_\perp$ is almost non-existent, which is an unusual result since for an elongated molecule we expect $E_\perp^{\mathrm{a}} > E_\parallel^{\mathrm{a}}$. In all other respects the agreement between experiment and this model for the spectral densities is acceptable. The value of A_{DF} is found to be $55 \pm 1\,\mathrm{s}^{-1}$, and for the axial deuterons the contribution of $J_1^{\mathrm{DF}}(\omega_0)$ is of the order of 50 per cent of the total, whereas for the equatorial deuterons it is only about 16 per cent.

The reason why $D_\perp$ is found to be temperature-independent may be because the model that we have used for the diffusional motion is too restricted. Thus Vold and Vold [14] have pointed out that the model for small-step rotational diffusion that characterizes the motion by two rotational diffusion constants for a cylindrical molecule does not correctly predict the ratios $J_1(\omega_0)/J_2(\omega_0)$ for deuterons either in small molecules dissolved in nematic solvents, or in mesogens themselves. They propose an alternative description of the diffusional motion that expresses the correlation function in equation (11) in terms of the individual Euler angles $\Omega_{LM} \equiv \alpha, \beta, \gamma$; thus

$$\begin{aligned}\overline{D^2_{m_Mm_L}(\Omega_{LM}(0))D^2_{m_Mm_L}(t)^*} &= \overline{D^2_{m_Mm_L}(\gamma(0))D^2_{m_Mm_L}(\gamma(t))^*}\\ &\quad\times \overline{D^2_{m_Mm_L}(\alpha(0)\beta(0))D^2_{m_Mm_L}(\alpha(t)\beta(t))^*}\,.\end{aligned} \tag{16}$$

The angle γ represents rotation about the molecular z axis, and this motion, which is expected to be the most rapid, is assumed to be independent of the motion of the z axis about the director (α motion), or towards the director (β motion). Vold and Vold show that with this division of the molecular motion the correlation times $\tau^{(2)}_{m_Mm_L}$ become

$$(\tau^{(2)}_{m_Mm_L})^{-1} = k_{m_M} + \frac{D_\beta}{\beta^{(2)}_{m_Mm_L}} + m_L^2(D_\alpha - D_\beta), \tag{17}$$

where k_{m_M} is determined by the nature of the γ motion. Thus

$$\left.\begin{aligned} k_0 &= 0,\\ k_2 &= (3p+1)k_1,\end{aligned}\right\} \tag{18}$$

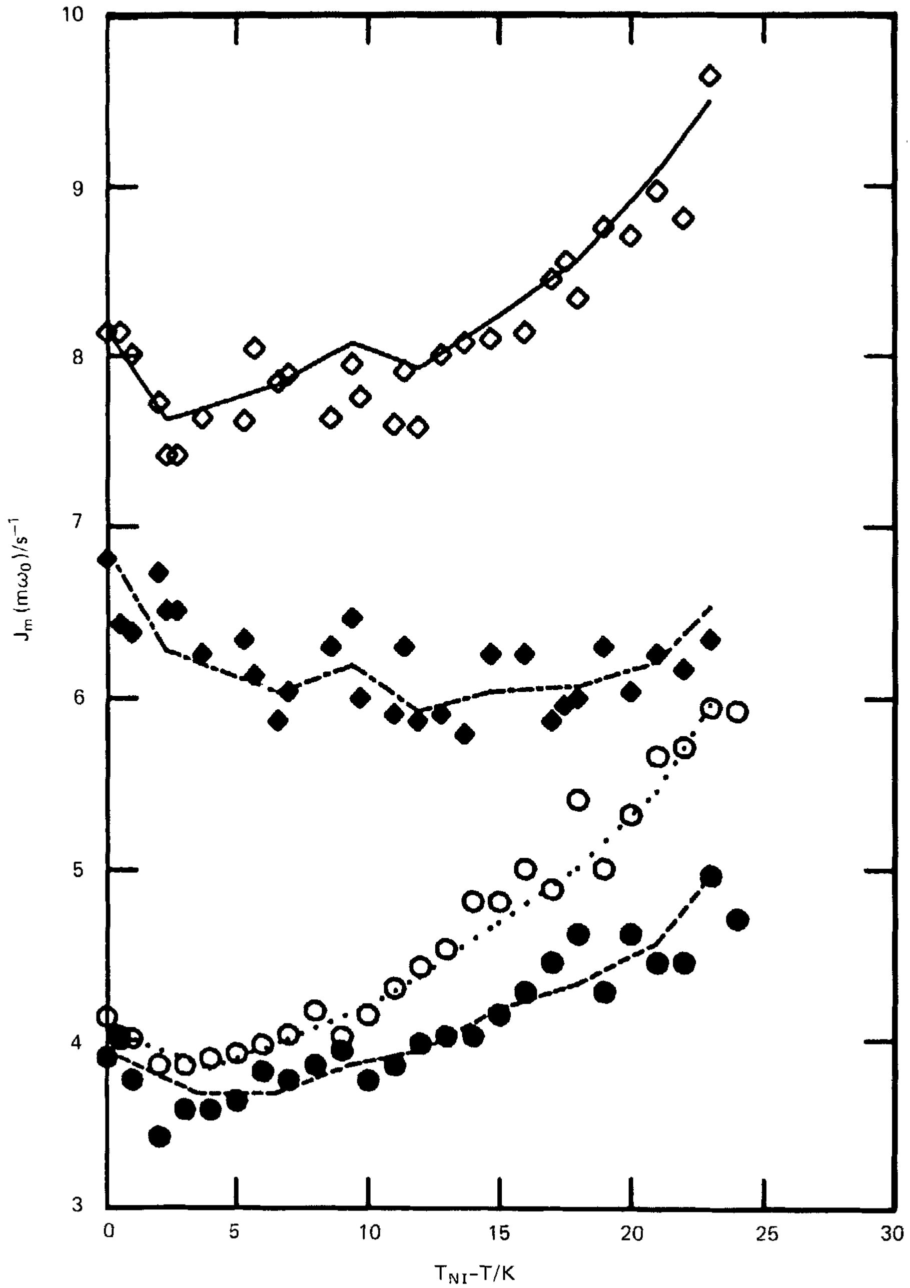

Figure 5. Spectral densities for deuterons at axial and equatorial positions in CCH3. The symbols denote the measured values (◇, $J_1^{ax}(\omega_0, 90°)$; ◆ $J_2^{ax}(2\omega_0, 90°)$; ○, $J_1^{eq}(\omega_0, 90°)$; ●, $J_2^{eq}(2\omega_0, 90°)$) and the continuous lines are those calculated with the model of relaxation as small-step rotational diffusion plus director fluctuations and connect calculated points.

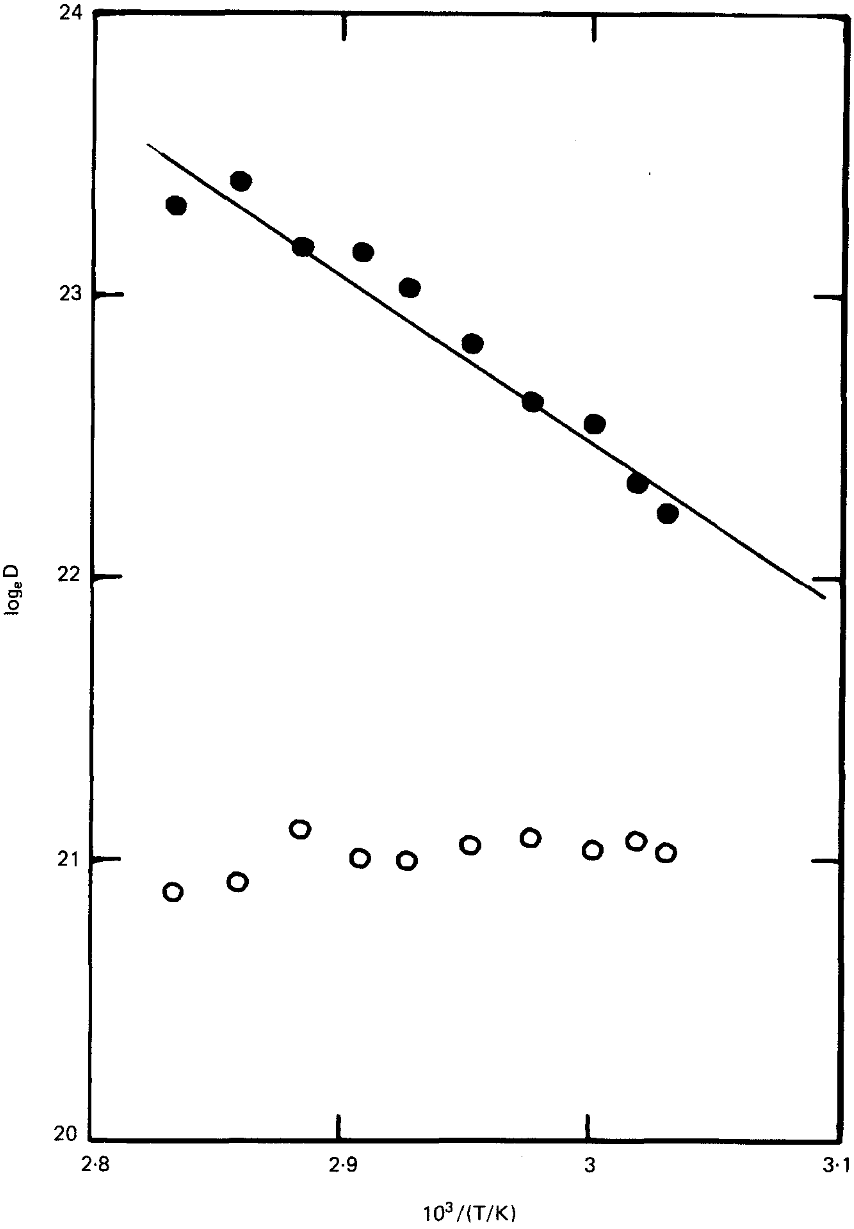

Figure 6. Temperature dependences of the rotational diffusion constants $D_{\parallel}$ (●) and $D_{\perp}$ (○) obtained from the model of relaxation as small-step rotational diffusion plus director fluctuations. The straight line is the result of a least-squares fit of $D_{\parallel}$ to an Arrhenius equation.

with $p = 0$ corresponding to strong collision and $p = 1$ to small-step rotational diffusion. There are therefore four variables describing the rotational motion, D_α, D_β, k_1 and p, and, since we expect director fluctuations to be important, the constant A_{DF} must also be included as an adjustable parameter with which to bring observed and calculated spectral densities into agreement. To reduce the number of adjustable

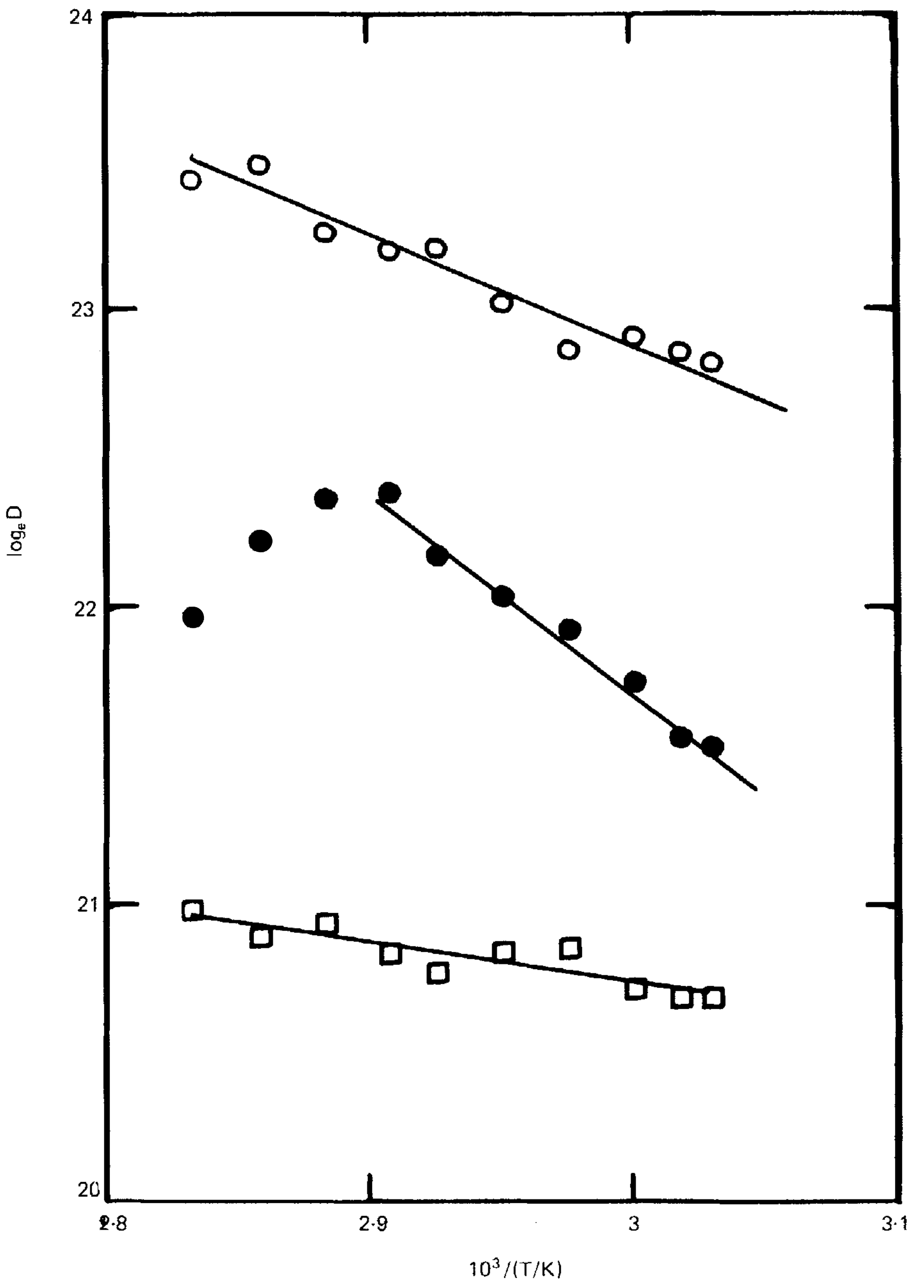

Figure 7. Temperature dependences of the rotational diffusion constants D_α (●), D_β (□) and D_γ (○). The straight lines are the results of least-squares fitting of the data to an Arrhenius equation.

parameters to match the number of observed spectral densities for CCH3-d_6, we set $p = 0$ and determine the values of $D_\gamma = k_1$, D_α, D_β and A_{DF} that fit the four spectral densities. The values of A_{DF} is found to have a small temperature dependence, decreasing from $52\,s^{-1}$ close to T_{NI} to $46\,s^{-1}$ at $T_{NI} - T = 23$ K. Thus both models for the motion predict that director fluctuations are an important relaxation process, particularly for axial deuterons.

The temperature dependences of the three rotational diffusion coefficients are shown in figure 7. Both D_γ and D_β obey an Arhenius relationship over the temperature range studied, giving activation energies for these rotational motions of $E_\gamma = 29\cdot5 \pm 2\cdot5\,\mathrm{kJ\,mol^{-1}}$ and $E_\beta = 11\cdot2 \pm 1\cdot8\,\mathrm{kJ\,mol^{-1}}$. The γ motion is an order of magnitude faster than the β motion, which is consistent with the smaller displacement of the nuclear masses when the molecule rotates about its approximate symmetry axis compared with motion of this axis towards the director. The magnitude of D_α is also considerably less than D_γ, but in this case an Arrhenius equation describes the temperature dependence only when $T_{\mathrm{NI}} - T$ is greater than about 5 K, giving an activation energy $E_\alpha = 51\cdot5 \pm 3\cdot3\,\mathrm{kJ\,mol^{-1}}$. There is a marked deviation from Arrhenius behaviour for D_α as T_{NI} is approached, whose origin is not apparent from our data.

4. Conclusion

The four spectral densities that we have measured for the axial and equatorial deuterons have enabled us to test different models for the motion producing spin relaxation. It would appear from our results that director fluctuations are an important, but not dominant, mechanism of spin relaxation. We have not, however, been able to clearly distinguish between the two models proposed for the rotational motion of the molecule. Both the two-parameter ($D_\parallel$ and $D_\perp$) and three-parameter (D_α, D_β, D_γ) models provide an acceptable fit to the data, and it would clearly be an advantage to explore these models in more detail, and to do so will require that more experimental data be obtained. It would be very interesting to increase the number of site-specific spectral densities by examining a molecule containing more deuteriated sites, and in addition to collect data at other Larmor frequencies.

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