Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

NMR relaxation of rigid molecules in the nematic phase of a discotic liquid crystal

E. A. Joghems[a]; C. A. Biesheuvel[a]; J. Bulthuis[a]
[a] Department of Physical and Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands

To cite this Article Joghems, E. A. , Biesheuvel, C. A. and Bulthuis, J.(1993) 'NMR relaxation of rigid molecules in the nematic phase of a discotic liquid crystal', Liquid Crystals, 13: 3, 427 — 443
To link to this Article: DOI: 10.1080/02678299308026315
URL: http://dx.doi.org/10.1080/02678299308026315

LIQUID CRYSTALS, 1993, VOL. 13, NO. 3, 427–443

NMR relaxation of rigid molecules in the nematic phase of a discotic liquid crystal

by E. A. JOGHEMS*, C. A. BIESHEUVEL and J. BULTHUIS
Department of Physical and Theoretical Chemistry, Vrije Universiteit,
de Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

(*Received 27 November 1991; accepted 12 November 1992*)

Frequency and temperature dependent NMR relaxation measurements were performed on deuteriated benzene, pyrene and triphenylene dissolved in the nematic phase of a discotic liquid crystal. The results show a strong frequency dependence of the spectral densities. Based on the symmetries of the system and the usual model for director fluctuations this frequency dependence should be equal for J_1 and J_2. From fitting the commonly used model of rotational diffusion and director fluctuations to the data we see that this is not the case for benzene and triphenylene, even though the fits themselves are satisfactory. Values for the elastic constants, effective viscosity and translational diffusion in similar discotic liquid crystals do not account quantitatively for the frequency dependence of benzene. For both pyrene and triphenylene quantitative comparison was impossible due to lack of translational diffusion data. We also find that the so-called cut-off wavelength is of the order of the dimensions of the liquid crystal molecules, just as in ordinary nematics.

1. Introduction

In ordinary, rod-like, thermotropic nematic liquid crystals, NMR relaxation experiments have shown the relaxation rates to depend on the field strength [1–4]. This is in sharp contrast to spin relaxation in ordinary liquids. The explanation usually given is that fluctuations in the preferred direction of the liquid crystal molecules (director) modulate the orientational movement of the (probe) molecule [5, 6]. Since these fluctuations are relatively slow compared to the normal tumbling rates of molecules they contribute to the low frequency part of the spectral densities. These spectral densities in turn determine the spin relaxation rates.

The director is defined as the average of the orientation of the liquid crystal molecules over a volume element containing a large number of these molecules. This imposes a problem when the wavelength of fluctuations is short compared to the dimensions of a single liquid crystal molecule. The usual way around this is to introduce a cut-off wavelength [3, 7]. We would hope that the precise value of this wavelength is unimportant, and large compared to a liquid crystal molecule. Relaxation experiments in rod-like nematics have shown, however, that its value is significant and of the order of the length of one such molecule [4, 8, 9]. In a discotic liquid crystal the director fluctuation contribution could be different, because of the disc-like shape of the molecules. This may result in a different cut-off wavelength. It is, therefore, of interest to extend measurements to discotic liquid crystals.

---

* Author for correspondence.

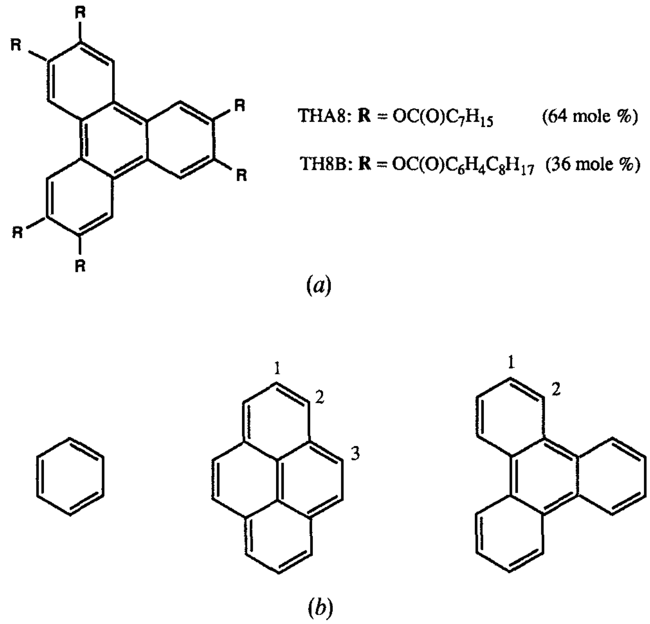


Figure 1. Molecules making up the discotic liquid crystal (*a*) and the probe molecules (*b*) from left to right benzene, pyrene and triphenylene. The deuterons 1 for pyrene are denoted by a *p* (for *para*) in the text, 2 and 3 by an r.

As in earlier experiments, we have studied the director fluctuations indirectly through the relaxation behaviour of rigid probe molecules dissolved in the liquid crystal. In this way contributions to the spectral densities arising from the internal dynamics of the liquid crystal molecules are avoided. The probe molecules used are benzene, pyrene and triphenylene (see figure 1). In the order given they are of increasing size, but of similar shape as the core of the discotic molecules, i.e. disc-like. The reason for using molecules of increasing size is that the interaction strength with the molecular field will also increase, as is evident from the enhancement of the order parameter. Consequently the effect of director fluctuations will be more pronounced. The largest probe molecule, triphenylene, has the same dimensions as the core. Attempts to use coronene, an even larger molecule, failed since it does not dissolve in the discogen.

2. Experimental

The discotic that was used is a mixture of THA8 and TH8B (see figure 1) and was synthesized in our laboratory, following a modification of the procedure of Nguyen Huu Tinh *et al.* [10]. According to the literature [11] this mixture has a nematic phase; this was confirmed by the textures observed between crossed polarizers. The nematic–isotropic transition temperature thus obtained was 356 K. However, the clearing point of the bulk sample was observed at the much higher temperature of 370 K. When probe molecules were added to the discotic the clearing point agreed, within experimental error, with the transition temperature as observed by NMR. Therefore we assume the observed clearing point, the more accurate of the two, to be equal to the transition temperature, T_{NI}; values for T_{NI} are given in table 1.

All three (deuteriated) probe molecules are commercially available and were used without further purification. In all cases about 3 wt% of probe molecules was added to

Table 1. Nematic–isotropic transition temperatures, temperature at which the frequency dependence of the spectral densities is shown (see figure 6) and the magnitude of the order parameters at this temperature.

Probe	T_{NI}/K	T/K	$\lvert S_{z'z'}\rvert$	$\lvert S_{x'x'}-S_{y'y'}\rvert$
Benzene	364	338	0·03	
Pyrene	363	349	0·096	0·017
Triphenylene	364	345	0·102	

the discotic in a standard 5 mm NMR tube previously cleaned with aqua regina and ethanol. After several freeze–pump–thaw cycles the tube was sealed. The tube was then put into an oven ($T > T_{NI}$) for several days. Because the fluid is very viscous a homogeneous mixture is not easily obtained. This can be improved by locally heating the sample while continually changing the orientation of the tube, so that the fluid is allowed to move along its sides. During the time the tube was placed in the oven this mixing procedure was repeated every now and again. If this is not done, the first few relaxation experiments will not lead to reproducible results. Prior to measurement, the mixing procedure was repeated. After this the sample was heated until it was in the isotropic phase, and left to cool to the required temperature inside the NMR magnet.

Since the probe molecules are deuteriated, the predominant relaxation mechanism is quadrupolar relaxation. The relaxation rates were measured using the Jeener–Broekaert pulse sequence with phase cycling as described by Vold *et al.* [12, 13]. This phase cycling ensures the disappearance of unwanted double and single quantum coherences. After the spin system has been put in a non-equilibrium state by the first two pulses of the sequence its relaxation is observed by applying a detection pulse after some time t. In the NMR spectra then observed, each deuteron gives rise to a doublet due to incomplete averaging of the quadrupolar coupling. The intensity of the two lines of this doublet, here named 1 and 2, depend on the time t as.

$$M_1 = A\exp(-R_z t) - B\exp(-R_q t), \qquad (1\,a)$$

$$M_2 = A\exp(-R_z t) + B\exp(-R_q t), \qquad (1\,b)$$

where A and B are constants determined by the initial state. By respectively adding and subtracting M_1 and M_2, the Zeeman and quadrupolar relaxation rates, R_z and R_q, can be obtained. The spectral densities can then be calculated from

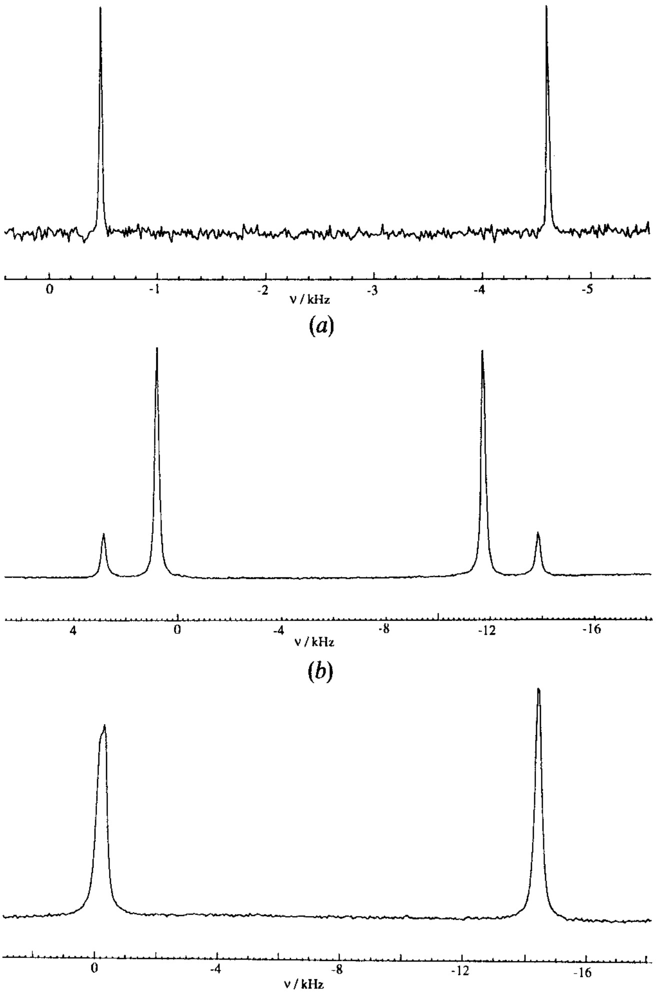
$$J_1 = \frac{R_z}{3c}, \qquad (2\,a)$$

$$J_2 = \frac{R_q}{4c} - \frac{R_z}{12c}, \qquad (2\,b)$$

where $c = \frac{3}{2}\pi^2(qcc)^2$, qcc being the quadrupolar coupling constant, defined later, for the deuteron of interest.

3. Order parameters

The NMR spectra of the three molecules in the discotic mixture are shown in figure 2. The spectrum for benzene is similar to that obtained by Goldfarb *et al.* [11] for benzene in a discotic liquid crystal in its nematic phase. To understand the spectra one



(*a*)

(*b*)

(*c*)

Figure 2. Spectra of benzene (*a*), pyrene (*b*) and triphenylene (*c*) dissolved in the nematic phase of a discotic liquid crystal.

order parameter is needed for benzene and triphenylene, and two for pyrene [14]. This is a consequence of the fact that benzene has six-fold-, and triphenylene three-fold symmetry about the axis perpendicular to the molecular plane, but pyrene has only two-fold symmetry. This axis of symmetry is chosen as the molecular z axis (called z' in figure 4). For benzene and triphenylene the order parameter is defined as $S_{z'z'} = \langle D^2_{00}(\Psi)\rangle$, where D^L_{jk} is a Wigner rotation matrix [15] and Ψ represents the Euler angles defining the orientation of the molecule with respect to the laboratory frame. This order parameter is related to the observed line splitting by

$$\Delta\nu = -\tfrac{3}{4}(qcc)S_{z'z'}, \tag{3}$$

where $qcc = (eQV^{1}_{z''z''})/h$ is the quadrupolar coupling constant, eQ is the deuterium quadrupole moment, and $V^{l}_{z''z''}$ is the electric field gradient in the local frame of the deuteron (see figure 4). The spectrum of benzene consists of a single doublet since all deuterons are equivalent. The triphenylene spectrum has one narrow and one broad line. The reason is that the two distinct deuterons (1 and 2 in figure 1) have slightly different quadrupolar couplings and chemical shifts. This gives rise to two quadrupolar doublets which do not completely coincide. The spectrum can be simulated by taking each observed line as the sum of two lorentzians of equal width which are shifted slightly. From the displacement of the two doublets relative to each other the difference in *qcc* and in chemical shift can be calculated. Good fits were obtained by taking the chemical shift difference to be about 1 ppm and the difference in *qcc* about 1 per cent. These numbers agree with values found in the literature [16].

The additional order parameter for pyrene is defined by

$$S_{x'x'}-S_{y'y'}=\sqrt{\tfrac{3}{2}}\langle D^2_{02}(\Psi)+D^2_{0-2}(\Psi)\rangle; \tag{4}$$

it is related to the line splitting for the different deuterons by

$$\Delta\nu_p=-\tfrac{3}{4}(qcc)[S_{z'z'}-(S_{x'x'}-S_{y'y'})], \tag{5a}$$

$$\Delta\nu_r=-\tfrac{3}{4}(qcc)[S_{z'z'}+\tfrac{1}{2}(S_{x'x'}-S_{y'y'})], \tag{5b}$$

where (p) applies to the *para* deuterons (1) and (r) to the remaining deuterons (2, 3). The two outer lines in the pyrene spectrum stem from the para deuterons, the inner lines from the remaining ones. Both the chemical shift and *qcc* are virtually equal for deuterons 2 and 3 so that no extra splitting is observed.

In figure 3 we have plotted the magnitude of the order parameters for the probe molecules as a function of temperature, assuming $qcc=186$ kHz for all deuterons. Previously, Goldfarb *et al.* [11] plotted the temperature dependence of the quadrupolar splitting for deuteriated benzene dissolved in the same discotic mixture.

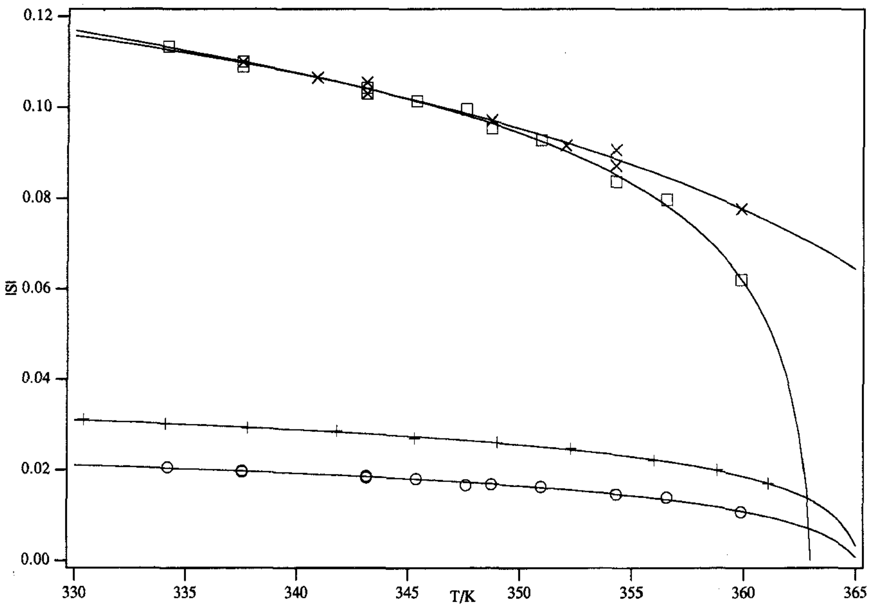


Figure 3. Magnitude of the order parameter, $S_{z'z'}$, as a function of temperature for benzene (+), pyrene (□) and triphenylene (×) in a nematic discotic. In addition $S_{x'x'}-S_{y'y'}$ is plotted for pyrene (○). The lines are fits to $a\ln(T^*-T)+b$.

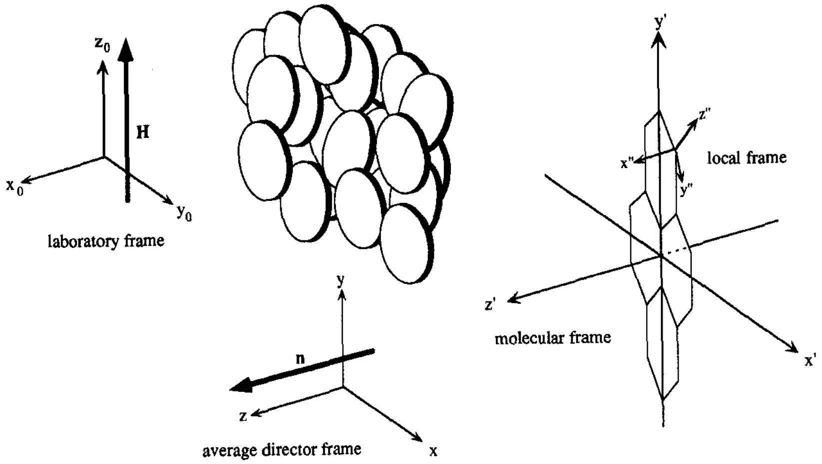


Figure 4. The different reference frames. The laboratory frame, on the left, has its z axis parallel to the external magnetic field. In the middle is an artist's impression of a small part of the discotic liquid crystal in this field. Below this the average director frame, which is perpendicular to the magnetic field. On the right, the molecular frame of the probe molecule ($'$) and the local frame ($''$) of a deuteron, drawn for pyrene.

Comparing their results with ours we find perfect agreement. They identified this temperature dependence as typical for a nematic phase. This is further evidence that we are dealing with a discotic nematic phase.

4. Spectral densities

Figure 5 shows the spectral densities J_1 and J_2 as a function of temperature at different NMR frequencies. Here we concentrate on the effects of director fluctuations. Extracting information about these from the data directly is rather awkward unless the temperature dependence of several physical constants of the liquid crystal is known from independent measurements. Since this is not the case, fit parameters must be used to model this temperature dependence. However, slow relaxation mechanisms, like director fluctuations, are observed mainly through the change of the spectral densities with frequency. Thus, by considering the spectral densities as a function of frequency at constant temperature, a large number of fit parameters can be eliminated. For each frequency, a value for J_1 and J_2 was obtained at the same temperature (see table 1), by interpolation. The results are shown in figure 6 and given in table 2. To interpret these data a model for the molecular motion is needed.

In the following we use several different reference frames; these are shown in figure 4. The discotic molecules orient with their molecular plane parallel to the magnetic field. This means no unique average director can be defined. We assume, however, that in a microscopically large domain the average director is constant during a measurement, and perpendicular to the applied magnetic field. The existence of such domains is indicated by the spectra observed by Goldfarb *et al.* [17] for deuteriated benzene in THE6. When they rotated their sample with respect to the magnetic field they obtained spectra typical of two dimensional powders. Since the spectra changed with the rotation angle, the director field adapts slowly to the new field direction. From this it may be concluded that the average director is indeed constant during one relaxation measurement, which is of the order of seconds at most. Further indication of the existence of these domains is given by the long time the sample remains in the liquid crystal phase after it is removed from the magnet and left at room temperature. The frame defined by the average director will be called the director frame. We assume axially symmetric motion of the probe molecule with respect to this frame.

The spectral densities in the laboratory frame J can be expressed in terms of those in the director frame J^{d}, through transformation by Wigner rotation matrices, as

$$J_1 = \tfrac{1}{2}J^{\mathrm{d}}_1 + \tfrac{1}{2}J^{\mathrm{d}}_2, \tag{6 a}$$

$$J_2 = \tfrac{3}{8}J^{\mathrm{d}}_0 + \tfrac{1}{2}J^{\mathrm{d}}_1 + \tfrac{1}{8}J^{\mathrm{d}}_2. \tag{6 b}$$

The J^{d}s depend on both the motion of the molecule and the position of the deuteron in the molecule, i.e. the local frame. For all three probe molecules we assume the motion to be axially symmetric about the molecular z axis (perpendicular to the molecular plane, see figure 1). In the case of pyrene this is incorrect since two order parameters are needed. We expect, however, that this has only a slight effect on the motion of the probe molecule, because the magnitude of the additional order parameter is relatively small. We now make a second transformation, from the molecular frame to the local frame. Then the J^{d}s can be written in terms of J^{m}s as

$$J^{\mathrm{d}}_k = \tfrac{1}{4}J^{\mathrm{m}}_{k0} + \tfrac{3}{8}(J^{\mathrm{m}}_{k2} + J^{\mathrm{m}}_{k-2}), \tag{7}$$

where J^{m}_{kl} is the real part of the Fourier transform of the correlation function

$$C^{\mathrm{m}}_{kl}(t) = \langle D^{2*}_{kl}(\Omega_0) D^2_{kl}(\Omega_t)\rangle \tag{8}$$

and Ω stands for the Euler angles defining the molecular frame with respect to the director frame. J^{m}_{kl} only depends on the motion of the molecule with respect to the average director frame, i.e. it is independent of the position of the deuteron in the molecule. Combining equations (6) and (7) gives

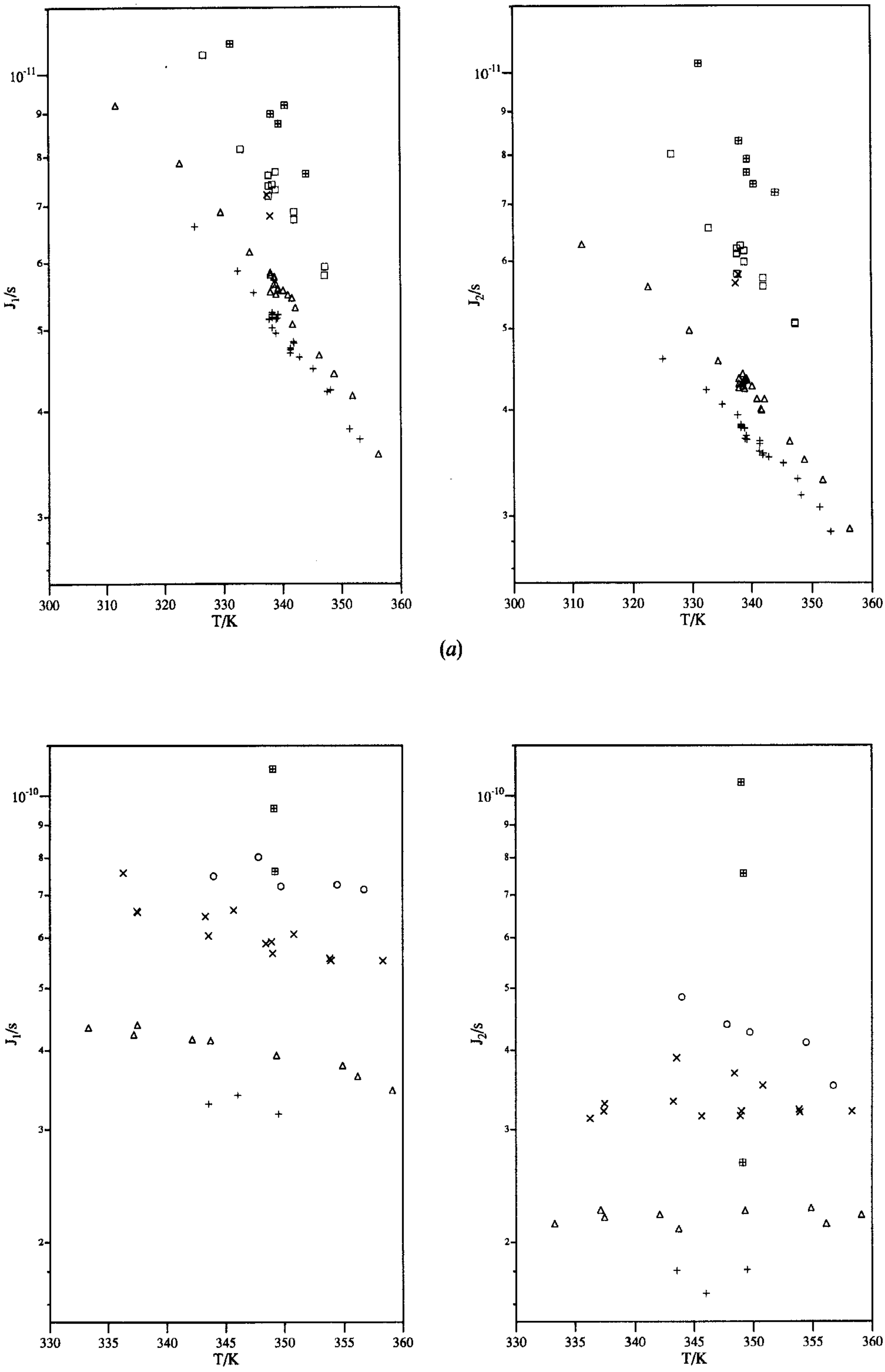
$$J_1 = \tfrac{1}{8}(J^{\mathrm{m}}_{10} + J^{\mathrm{m}}_{20}) + \tfrac{3}{16}(J^{\mathrm{m}}_{12} + J^{\mathrm{m}}_{1-2} + J^{\mathrm{m}}_{22} + J^{\mathrm{m}}_{22} + J^{\mathrm{m}}_{2-2}), \tag{9 a}$$

$$\begin{aligned} J_2 = {} & \tfrac{1}{32}(3J^{\mathrm{m}}_{00} + 4J^{\mathrm{m}}_{10} + J^{\mathrm{m}}_{20}) + \tfrac{1}{64}(9J^{\mathrm{m}}_{02} + 9J^{\mathrm{m}}_{0-2} + 12J^{\mathrm{m}}_{12} \\ & + 12J^{\mathrm{m}}_{1-2} + 3J^{\mathrm{m}}_{22} + 3J^{\mathrm{m}}_{2-2}). \end{aligned} \tag{9 b}$$

At this point we need to specify a model for the motion of the probe molecules in the liquid crystal. We use the widespread and relatively simple model of isotropic rotational diffusion in a fluctuating potential resulting from director fluctuations [7]. Even though the probe molecules are not spherical, and therefore isotropic rotational diffusion seems too simple, this model is adequate for our purposes. This is because in the extreme narrowing limit, i.e. $\omega^2\tau_{\mathrm{R}}^2 \ll 1$, the frequency dependent terms, caused by director fluctuations, are insensitive to the details of the motion about the director. Thus, refining the model to incorporate more realistic rotational diffusion will lead to extra contributions which are independent of frequency. This would only be useful if it were possible to obtain direct data on the frequency independent terms, otherwise it will result in extra fit parameters.

For this model, the spectral densities, J^{m}_{kl}, are

$$J^{\mathrm{m}}_{kl}(\omega) = \langle D^{2*}_{kl} D^2_{kl}\rangle \frac{\tau_{\mathrm{R}}}{1+\omega^2\tau_{\mathrm{R}}^2} + \frac{3}{2}\sqrt{\left(\frac{\pi}{2}\right)} S^2 A \left\{\frac{u(\omega_{\mathrm{c}}/\omega)}{\sqrt{\omega}} - \frac{2}{\pi}\frac{\sqrt{(2\omega_{\mathrm{c}})}\tau_{\mathrm{R}}}{1+\omega^2\tau_{\mathrm{R}}^2}\right\}\delta_{k,\pm 1}\delta_{l,0}, \tag{10}$$


10^{-11}
9
8
7
6
5
4
3
J_1/s
300
310
320
330
340
350
360
T/K
10^{-11}
9
8
7
6
5
4
3
J_2/s
300
310
320
330
340
350
360
T/K
10^{-10}
9
8
7
6
5
4
3
2
J_1/s
330
335
340
345
350
355
360
T/K
10^{-10}
9
8
7
6
5
4
3
2
J_2/s
330
335
340
345
350
355
360
T/K

(*a*)

(*b*)

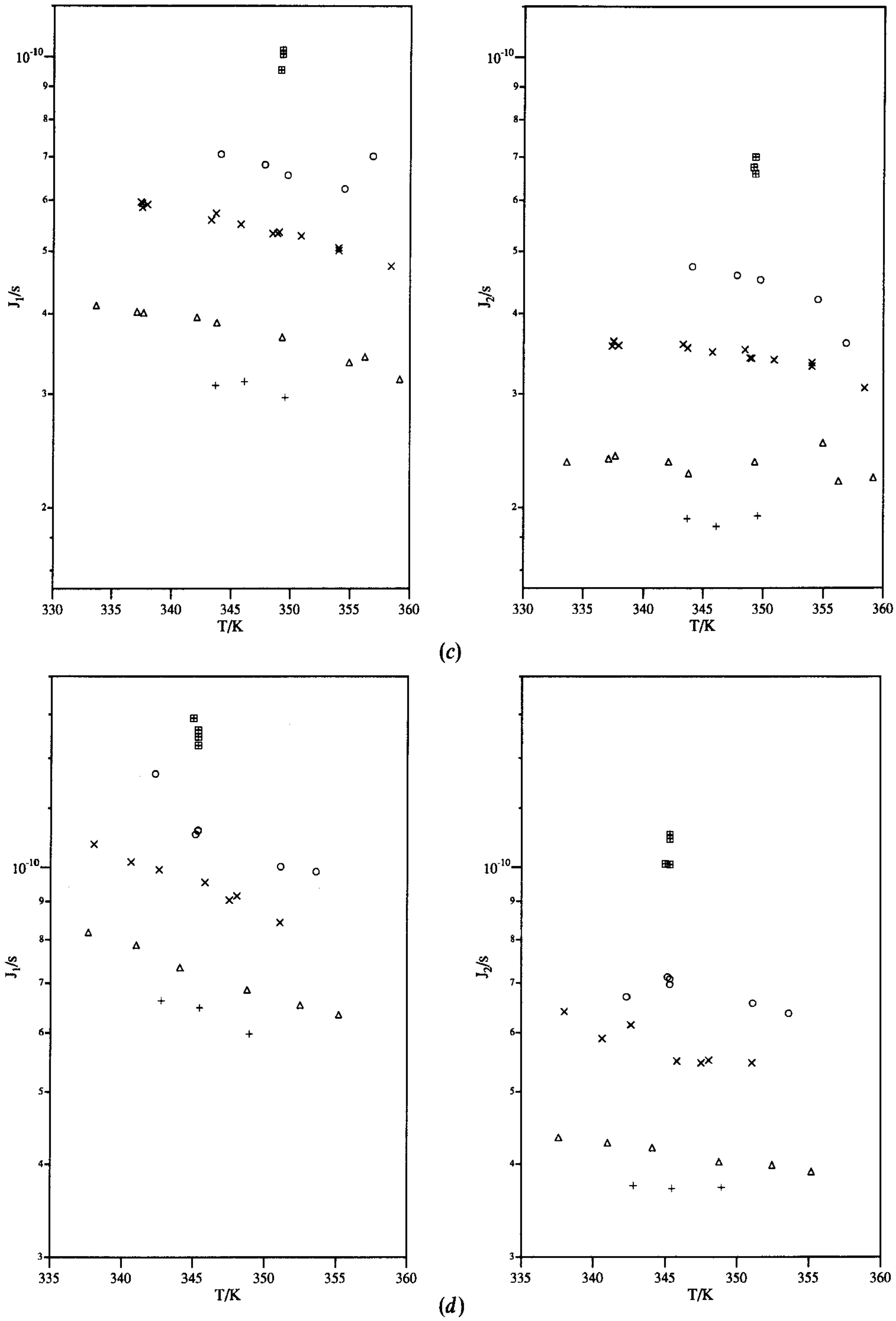
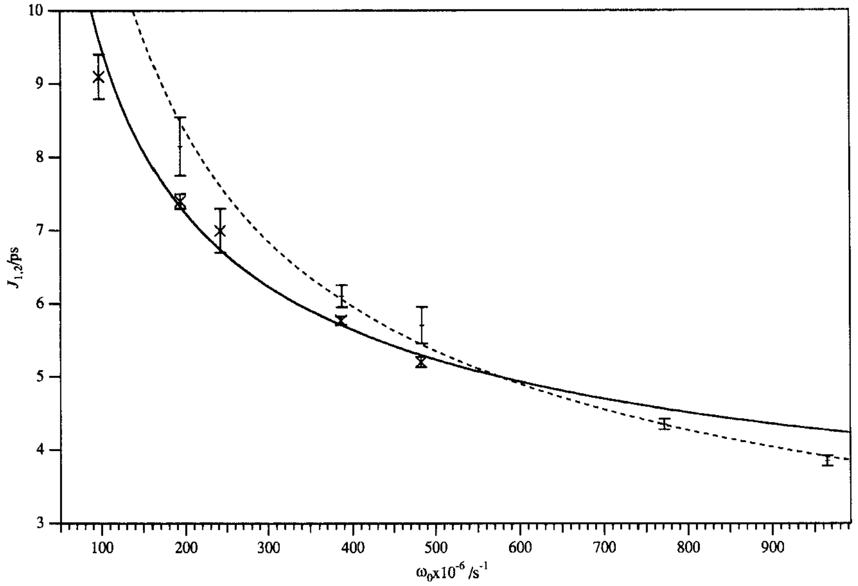
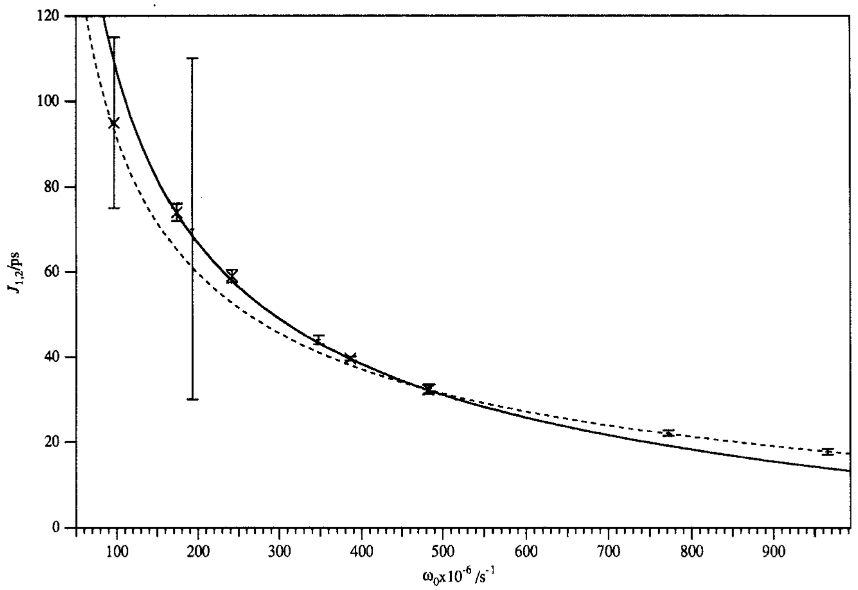


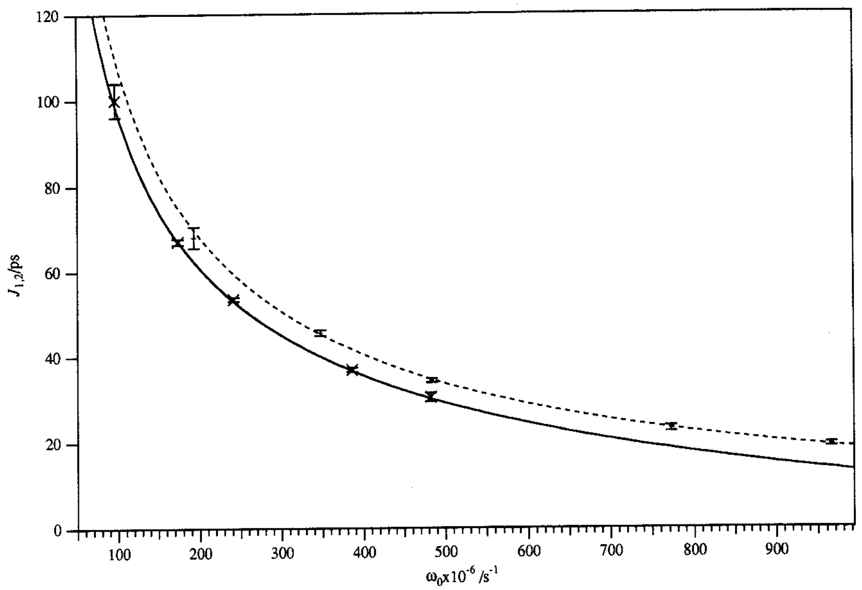
Figure 5. Spectral densities J_1 and J_2 for benzene (*a*), pyrene (*para* (*b*), others (*c*)) and triphenylene (*d*) as a function of temperature, at NMR frequencies 15·39 MHz (⊞), 27·66 MHz (○), 30·77 MHz (□), 38·48 MHz (×), 61·42 MHz (△), 76·78 MHz (+). Error bars have been omitted for clarity. (All data, including estimated errors, are available from the authors upon request.)


$J_{1,2}$/ps
10
9
8
7
6
5
4
3
100
200
300
400
500
600
700
800
900
ω_0x10^{-6} /s^{-1}

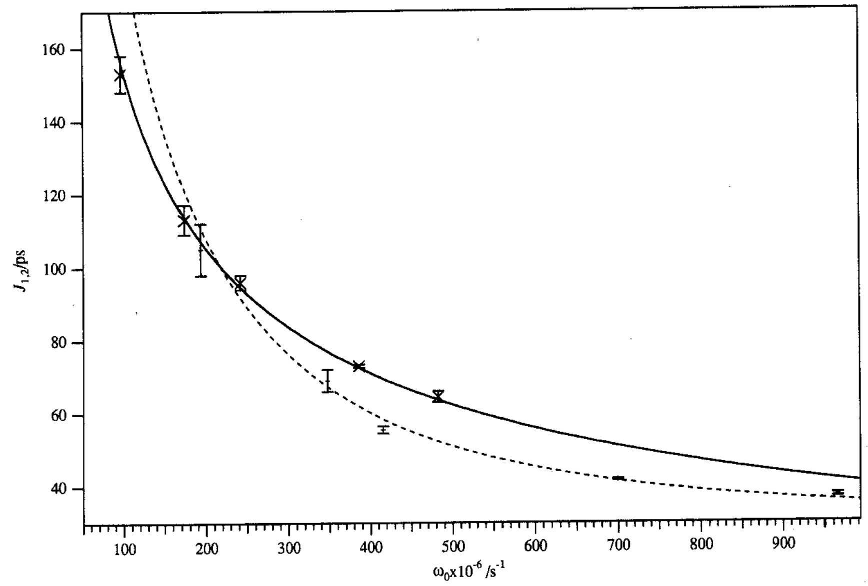
(*a*)


$J_{1,2}$/ps
120
100
80
60
40
20
0
100
200
300
400
500
600
700
800
900
ω_0x10^{-6} /s^{-1}

(*b*)



(c)



(d)

Figure 6. Spectral densities J_1 (×) and J_2 (+) for benzene (*a*), pyrene (*para* (*b*), remaining deuterons (*c*)) and triphenylene (*d*) as a function of the NMR frequency at a constant temperature. The solid lines is the fit for J_1, the dashed line for J_2.

Table 2. (*a*) Spectral densities for benzene at 338 K. The figures in parentheses are the estimated errors.

ν_0/MHz	J_1/ps		J_2/ps	
15·39	9·1	(0·3)	8·15	(0·4)
30·77	7·4	(0·1)	6·1	(0·15)
38·48	7·0	(0·3)	5·7	(0·25)
61·42	5·77	(0·06)	4·35	(0·07)
76·78	5·20	(0·07)	3·85	(0·07)

Table 2. (*b*) Spectral densities for pyrene at 349 K. *p* denotes the para deuterons and *r* the remaining deuterons.

ν_0/MHz	J_1^p/ps		J_2^p/ps		J_1^r/ps		J_2^r/ps	
15·39	95	(20)	70	(40)	100	(4)	68	(2·5)
27·66	74	(2)	44·1	(1)	67	(0·7)	45·5	(0·7)
38·48	59	(1·5)	32·4	(1)	53·5	(0·5)	34·4	(0·5)
61·42	39·6	(0·5)	21·9	(0·7)	36·9	(0·5)	23·0	(0·5)
76·78	32·3	(1)	17·8	(0·7)	30·5	(1)	19·2	(0·5)

Table 2. (*c*) Spectral densities for triphenylene at 345 K.

ν_0/MHz	J_1/ps		J_2/ps	
15·39	153	(5)	105	(7)
27·66	113	(4)	69	(3)
38·48	96	(2)	55·5	(1)
61·42	73	(0·5)	41·6	(0·2)
76·78	64·5	(1·5)	37·2	(0·5)

with

$$u(x)=\frac{1}{\pi}\left[\tfrac{1}{2}\ln\left(\frac{1-\sqrt{(2x)}+x}{1+\sqrt{(2x)}+x}\right)+\arctan(\sqrt{(2x)}+1)+\arctan(\sqrt{(2x)}-1)\right], \qquad (11)$$

$$A=\frac{kT}{2\pi^{3/2}K}\left(\frac{K}{\eta}+D_{\mathrm{tr}}\right)^{-1/2}, \qquad (12)$$

$$\omega_{\mathrm{c}}=\left(\frac{2\pi}{\lambda_{\mathrm{c}}}\right)^2\frac{K}{\eta}, \qquad (13)$$

where $\langle D_{kl}^{2*}D_{kl}^2\rangle$ is an equilibrium average and $\tau_{\mathrm{R}}=1/6D$ is the rotational diffusion correlation time (D is the effective rotational diffusion constant), K an elastic constant (one constant approximation), η an effective viscosity [18], D_{tr} the translation diffusion constant for the probe molecules (assumed isotropic), and λ_{c} the cut-off wavelength referred to previously. Substituting equation (10) into (9) gives, in the extreme narrowing limit

$$J_1(\omega)=\tfrac{1}{8}(\kappa_{10}+\kappa_{20}+3\kappa_{12}+3\kappa_{22})\tau_{\mathrm{R}}+\frac{3}{16}\sqrt{\left(\frac{\pi}{2}\right)}S^2A\left\{\frac{u(\omega_{\mathrm{c}}/\omega)}{\sqrt{\omega}}-\frac{2}{\pi}\sqrt{(2\omega_{\mathrm{c}})}\tau_{\mathrm{R}}\right\}, \qquad (14\,a)$$

$$J_2(\omega)=\tfrac{1}{32}(3\kappa_{00}+4\kappa_{10}+\kappa_{20}+9\kappa_{02}+12\kappa_{12}+3\kappa_{22})\tau_R$$
$$+\frac{3}{16}\sqrt{\left(\frac{\pi}{2}\right)}S^2A\left\{\frac{u(\omega_c/\omega)}{\sqrt{\omega}}-\frac{2}{\pi}\sqrt{(2\omega_c)}\tau_R\right\}. \tag{14b}$$

Values of $\kappa_{kl}=\langle D^2_{kl}D^2_{kl}\rangle$, for isotropic diffusion in a second rank potential of mean torque, depending on the order parameter S, are given in [19]; we also used $\kappa_{kl}=\kappa_{k-l}$. Here we note that the order parameter, S, used in equation (10) is defined with respect to the director frame. It is, therefore, twice as large and of opposite sign as the order parameters, $S_{z'z'}$, given in table 1. However, since it only enters the expressions squared, the sign of $S_{z'z'}$ is not important here.

5. Results and discussion

From equation (14) we see that both J_1 and J_2 can be fitted using the function

$$J_k(\omega)=\alpha_k+\beta\frac{u(\omega_c/\omega)}{\sqrt{\omega}}, \tag{15}$$

where

$$\beta=\frac{3}{16}\sqrt{\left(\frac{\pi}{2}\right)}S^2A \tag{16}$$

and α_k is the total frequency independent term, and thus incorporates the last term in both equations (14 *a*) and (14 *b*), the so-called cross-term. Notice that β, and therefore A, should be the same for both Js. Also note that for probes with low order, like benzene, $\alpha_k\approx\tau_R/5$. Fitting the spectral densities, independently, to these data gives us three parameters, α_k, β and ω_c. For the J_2 data of triphenylene, $\omega_c\approx 3\times 10^8\,\mathrm{s}^{-1}$ gives the best results. In all other cases values of ω_c ranging from about $10^9\,\mathrm{s}^{-1}$ to infinity give good fits. This is because these values of the cut-off are outside the range of measured frequencies, so that they have hardly any effect on the frequency dependent term, i.e. $u(\omega_c/\omega)\approx 1$ in this range.

From the fit parameter β, a value for A can be obtained using equation (16). For the different probes, the A values are given in the second and third column of table 3, from fits of J_1 and J_2, respectively. The error from the J_2 data of triphenylene is very large because A is sensitive to changes in ω_c when the latter is in the experimental frequency range. The frequency dependent contribution from director fluctuations is to J^m_{10}. Because of the symmetries of the system, J^m_{10} contributes to both J_1 and J_2 equally, as can be seen from equation (9). Therefore, the values for A obtained from both J_1 and J_2 should be the same, as noted previously. From table 3 it is seen that for benzene and triphenylene this is not the case, but for pyrene it holds quite well. An explanation for the observed difference of A cannot depend on the details of the rotational diffusion, which only contributes to the frequency independent part of the spectral densities. It should be sought in frequency dependence in J^m_{00} or J^m_{20}, not negligible compared to that in J^m_{10}. However, we then need a mechanism, differing from director fluctuations, with a long correlation time.

For all spectral densities, with the exception of J_2 for triphenylene, any value of ω_c larger than $10^9\,\mathrm{s}^{-1}$ may be chosen without affecting the quality of the fit. Contrary to A, however, the value of α_k does depend on this chosen value. This is because, in the extreme narrowing approximation, α_k is determined by the asymptotic behaviour of the spectral densities at infinite frequency. Since at the highest NMR frequency available to us the spectral densities still have a frequency dependent contribution, this asymptotic

Table 3. The parameter A, describing the effect of director fluctuations on the spectral densities, and some typical values of the frequency independent term, α_k. Both were obtained from fitting the spectral densities to equation (15). The figures in parentheses are estimated errors.

Probe	$A \times 10^6/s^{1/2}$ From J_1		$A \times 10^6/s^{1/2}$ From J_2		$\alpha_k \times 10^{12}/s$ for $\omega_c \approx 2 \times 10^9\,s^{-1}$
Benzene	94	(9)	143	(10)	1–3
Pyrene^r	142	(4)	143	(8)	4–8
Pyrene^p	161	(10)	141	(12)	4–8
Triphenylene	166	(10)	316	(100)	15–30†

^{p}: denotes the *para* deuterons, ^{r}: denotes the remaining deuterons.
† The high value comes from the J_2 data for which $\omega_c \approx 3 \times 10^8\,s^{-1}$.

behaviour is ill-defined. Values for ω_c at most an order of magnitude larger than the highest NMR frequency effectively raise the value found for α_k, with respect to its value for infinite ω_c. Some typical values for α_k for the different probe molecules are given in the fourth column of table 3, when ω_c is of the order of $2 \times 10^9\,s^{-1}$. We should remark here that the error in α_k is an order of magnitude larger than the values themselves. Even negative values of α_k were in some cases obtained from the fit, which is, of course, nonsensical. Since α_k is proportional to the rotational diffusion correlation time we expect the value of α_k to increase with probe size, which appears to be the case. From α_k the rotational diffusion correlation time, τ_R, can, in principle, be obtained. Its value depends, however, on the details of the rotational diffusion model used. Estimates for τ_R, based on the isotropic rotational diffusion model, obtained from α_k, varied wildly but remained well within the extreme narrowing limit, which justifies that assumption.

To evaluate the experimental results we compare the values for A in table 3 with those obtained from equation (12) by substituting literature values for the elastic constant, K, effective viscosity, η, and diffusion constant, D_{tr}. Unfortunately, few data on these quantities have been reported for discotics. Warmerdam *et al.* [20] found $K = 0{\cdot}5$–$8\,\mathrm{pN}$ and $\eta = 0{\cdot}05$–$0{\cdot}3\,\mathrm{kg\,m^{-1}\,s^{-1}}$ in other discotic triphenylene derivatives. Similar values have been reported by others [21, 22]. In those discotics the nematic–isotropic transition temperature is generally more than 100 K higher than in our sample. Since we have not found data for discotic nematics with lower transition temperatures we assume K and η to be of the same order of magnitude at the same reduced temperature. Also we assume that the addition of a small amount of probe molecules will not make much difference. Diffusion measurements of benzene in a similar discotic liquid crystal gave $D_{tr} = 1{\cdot}5$–$2{\cdot}5 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$ [23]. Using these values we find that for benzene $A = 2 - 70 \times 10^{-6}\,s^{1/2}$, which is smaller than the fitted values in table 3. The value of A is especially sensitive to D_{tr} since this is larger than K/η. We do have some reservations with respect to the values reported for D_{tr} in [23]. It has the same order of magnitude as in rod-like nematics [24–26] whereas the viscosity of discotics is much larger [22]. Also, no mention is made of the probe concentration, or change in transition temperature of the samples. Since for a large probe concentration the diffusion constant could increase appreciably, the value in our sample could be smaller. To get agreement with the values from our experiment the translational diffusion constant has to be less than half the lower value given here.

Evaluating A, based on independent measurements, for pyrene and triphenylene is more difficult since no data are available on their translational diffusion in discotics. Qualitatively we may argue that A will be larger due to slower diffusion, which is indeed observed. We can calculate an upper bound on the value of A assuming that the translational motion is negligible. Then, using the same values for K and η, we find that $A = 5\text{–}650 \times 10^{-6}\,\mathrm{s}^{1/2}$. This fairly broad range of values contains all experimental results. Good agreement with our data can be obtained when the translational diffusion is slow, i.e. $D_{\mathrm{tr}} < 3{\cdot}5 \times 10^{-11}\,\mathrm{m}^2\,\mathrm{s}^{-1}$. Using equation (13), with the values for K and η gives $\lambda_c = 5\text{–}50\,\text{Å}$ if $\omega_c = 2{\cdot}5 \times 10^{-8}\,\mathrm{s}^{-1}$ and $\lambda_c = 2{\cdot}5\text{–}25\,\text{Å}$ if we take $\omega_c = 10^9\,\mathrm{s}^{-1}$. Even larger ω_c will, of course, give smaller cut-off wavelengths. Restricting the range of values of K, η and ω_c to those which give values of A and α_k closest to those in table 3, we find $\lambda_c < 10\,\text{Å}$. This is of the dimensions of the discotic molecules.

From figure 6 (*a*) we see that the fits for the spectral densities of benzene increase faster with decreasing frequency than the data do. When we do not make the extreme narrowing approximation, but fit the results using

$$J_k(\omega) = \frac{a_k}{1 + \omega^2 \tau_k^2} + \beta \frac{1}{\sqrt{\omega}} \tag{17}$$

we find almost perfect fits for benzene. For pyrene and triphenylene they are only slightly different. In equation (17) we have assumed the cut-off frequency found from the fits using equation (15), i.e. much larger than the highest NMR frequency. The results of the fits, using equation (17), are given in tables 4 (*a*) and (*b*). From these we see that the values for A are somewhat smaller than those in table 3. For benzene the value from J_1 is now within the range calculated from the literature as indicated previously, but the value from J_2, is persistently larger. A is smaller because part of the frequency dependence is now included in the rotational diffusion term. Since the order parameters are small, especially for benzene, a_k should be about $\tau_k/5$. It is at least a factor of 50 smaller than this, which makes the result of these fits questionable. The influence, mentioned previously, of the value of the cut-off wavelength on the frequency independent term is negligible. When we take into account axially symmetric, instead of isotropic, rotational diffusion we win at most a factor of about five, so we are still off by more than an order of magnitude. We also note that the improvement in the benzene fits is largest, whereas we would expect the effect to be more pronounced for the larger, higher ordered, molecules pyrene and triphenylene. So, even though the fits for benzene are better, and the values for A are closer to the calculated ones, it is unreasonable to hide part of the frequency dependence in an unrealistic rotational diffusion term.

Apart from the separate fits for J_1 and J_2, they were fitted simultaneously using the SAS statistics package (Marquardt algorithm). The results of these fits agree with the values obtained from the independent fits. However, in this case the fitting procedure requires the relation between the frequency independent, rotational diffusion, parts of J_1 and J_2. Therefore a model with two diffusion constants, one for the motion of the axis and one for motion about the axis, is more appropriate. However, we have no measurements in the frequency regime where the spectral densities are constant, which already led to problems for a single rotational diffusion constant, so that an accurate estimate for the frequency independent terms cannot be made. Therefore a second rotational diffusion constant will only serve as an extra fit parameter. It will not provide better results, unless we have independent information about the relative magnitude of both constants.

Table 4. (*a*) Results of fits of J_1 data using equation (17).

Probe	$A \times 10^6/s^{1/2}$	$\tau_1 \times 10^9/s$	$a_1 \times 10^{12}/s$
Benzene	64 (13)	1·3 (0·3)	4 (1·5)
Pyrene^r	64 (10)	5·7 (3)	50 (7)
Pyrene^p	51 (20)	4 (1)	60 (10)
Triphenylene	136 (15)	4·3 (2)	22 (10)

^{p}: denotes the *para* deuterons, ^{r}: denotes the remaining deuterons.

Table 4. (*b*) Results of fits of J_2 data using equation (17).

Probe	$A \times 10^6/s^{1/2}$	$\tau_2 \times 10^9/s$	$a_2 \times 10^{12}/s$
Benzene	110 (26)	1·0 (0·2)	2 (1·5)
Pyrene^r	55 (3)	3·5 (0·4)	50 (5)
Pyrene^p	51 (15)	3·7 (2)	55 (20)
Triphenylene	111 (10)	32 (100)	610 (4×10^3)

^{p}: denotes the *para* deuterons, ^{r}: denotes the remaining deuterons.

6. Conclusions

Relaxation experiments on some rigid molecules dissolved in the nematic phase of a discotic liquid crystal show a large frequency dependence in the spectral densities J_1 and J_2. Since the director aligns perpendicular to the applied field, the usual description of director fluctuations means that the frequency dependent contributions to both J_1 and J_2 are equal. Therefore, no simple separation into contributions of rotational diffusion and director fluctuations can be made as in the case of parallel alignment. This, together with the persistence of the director fluctuation contribution up to the highest NMR frequency available to us, means no good estimate for the rotational diffusion contribution can be made. To acquire more insight into the rotational diffusion behaviour in discotics, the relaxation experiments would have to be extended to frequencies beyond those currently available for NMR.

The often used model of isotropic rotational diffusion and director fluctuations fits each of the spectral densities well. However, in contrast to what is expected, we find that for benzene and triphenylene the strength of the director fluctuation contribution, A, is different when obtained from fits of J_1 or J_2. For pyrene the values are much closer. We have, unfortunately, not been able to solve this problem. It may be used to advantage in future studies, as a test for models of molecular motion in liquid crystals. Irrespective of the inconsistency we see that all values obtained for A are an order of magnitude larger than in rod-like nematics, where $A = 2\text{–}10 \times 10^{-6}\,\mathrm{s}^{1/2}$ [4]. However, the values found in the literature for the elastic constant K, effective viscosity η, and translation diffusion constant D_{tr} in similar discotics cannot explain a value for A of $90\text{–}150 \times 10^{-6}\,\mathrm{s}^{1/2}$ for benzene. Quantitative comparison of the pyrene and triphenylene data in this way is impossible because no values for the translation diffusion constants are available.

As we have mentioned, a major topic of interest to us is the cut-off wavelength, λ_c, which plays such a critical role in rod-like nematics because it is of the order of the length of a single liquid crystal molecule. For the discotic studied here, we find that $\lambda_c < 10$ Å, for values of K and η which give best agreement with the experiment. This means that here too λ_c is of the order of molecular dimensions. Therefore, we cannot resolve questions concerning the cut-off, but find that for a nematic discotic phase the same difficulty with its length arises as in rod-like nematics.

We thank R. Lourens and R. Mooyman for the synthesis of the discotics molecules, J. Joordens and G. Nachtegaal of the SON HF-NMR facility at Nijmegen for their assistance, E. Biesheuvel for fitting the data using the SAS package, R. Stomphorst for critically reading of the manuscript, and G. van der Zwan for many stimulating discussions and his critical comments concerning the manuscript.

References

[1] DOANE, J. W., and VISINTAINER, J. J., 1969, *Phys. Rev. Lett.*, **23**, 1421.
[2] VILFAN, M., BLINC, R., and DOANE, M. W., 1972, *Solid St. Commun.*, **11**, 1073.
[3] UKLEJA, P., PIRS, J., and DOANE, J. W., 1976, *Phys. Rev.* A, **14**, 414.
[4] PLOMP, L., and BULTHUIS, J., 1988, *Liq. Crystals*, **3**, 927.
[5] PINCUS, P., 1968, *Solid St. Commun.*, **7**, 415.
[6] DOANE, J. W., and JOHNSON, D. L., 1970, *Chem. Phys. Lett.*, **6**, 291.
[7] FREED, J. H., 1977, *J. chem. Phys.*, **66**, 4183.
[8] DOANE, J. W., TARR, C. E., and NICKERSON, M. A., 1974, *Phys. Rev. Lett.*, **33**, 620.
[9] VOLD, R. R., VOLD, R. L., and SZEVERENYI, N. M., 1981, *J. phys. Chem.*, **85**, 1934.
[10] NGUYEN, HUU TINH, DUBOIS, J. C., MALTHETE, J., and DESTRADE, C., 1978, *C. r. hebd. Séanc. Acad. Sci., Paris*, C, **284**, 463.
[11] GOLDFARB, D., LUZ, Z., and ZIMMERMANN, H., 1982, *J. Phys., Paris*, **43**, 1255.
[12] VOLD, R. L., DICKERSON, W. H., and VOLD, R. R., 1981, *J. magn. Reson.*, **43**, 213.
[13] BARBARA, T. M., VOLD, R. L., and VOLD, R. R., 1984, *J. magn. Reson.*, **59**, 478.
[14] SHILSTONE, G. N., ZANNONI, C., and VERACINI, C. A., 1989, *Liq. Crystals*, **6**, 303.
[15] ZANNONI, C., 1985, *Nuclear Magnetic Resonance of Liquid Crystals*, edited by J. W. Emsley (NATO ASI Series, Vol. 141).
[16] LOHMAN, J. A. B., 1980, Thesis, Vrije Universiteit, Amsterdam, Chap. 1.
[17] GOLDFARB, D., LUZ, Z., and ZIMMERMANN, H., 1981, *J. Phys., Paris*, **42**, 1303.
[18] DE GENNES, P. G., 1974, *The Physics of Liquid Crystals* (Clarendon), Chap. 5.
[19] LIN, W., and FREED, J. H., 1979, *J. chem. Phys.*, **83**, 379.
[20] WARMERDAM, T. W., 1987, Thesis, Utrecht.
[21] MOUREY, B., PERBET, J. N., HARENG, M., and LE BERRE, S., 1982, *Molec. Crystals liq. Crystals*, **84**, 193.
[22] VERTOGEN, G., and DE JEU, W. H., 1988, *Thermotropic Liquid Crystals* (Springer-Verlag) (Springer Series in Chemical Physics).
[23] DONG, R. Y., GOLDFARB, D., MOSELEY, M. E., LUZ, Z., and ZIMMERMANN, H., 1984, *J. phys. Chem.*, **88**, 3148.
[24] MOSELEY, M. E., and LOEWENSTEIN, A., 1982, *Molec. Crystals liq. Crystals*, **90**, 117.
[25] KRÜGER, G. J., and SPIESECKE, H., 1971, *Ber. Buns. Ges. phys. Chem.*, **75**, 272.
[26] ZUPANCIC, I., PIRS, J., LUZAR, M., BLINC, R., and DOANE, J. W., 1974, *Solid St. Commun.*, **15**, 227.