Dynamics of Liquid Crystals by Means of ^{2}H-NMR: a Comparison between 4,4′-bis(hexyloxy)azoxybenzene and the Derivative Pd(II) Complex AZPAC *

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In the present work we report a molecular dynamics investigation of the two mesogens 4,4′-bis(hexyloxy)azoxybenzene (**HL**) and its Pd(II) acetylacetonate derivative **Azpac** in their nematic phases. Deuterium Zeeman and quadrupolar spin-lattice relaxation times have been measured at 46.04 MHz on two isotopomers of **Azpac** (**Azpac**-d_4 and **Azpac**-d_{26}, deuteriated on the aromatic core and on the alkoxy chains, respectively) and on **HL**-d_4, an isotopomer of **HL** partially deuteriated on the aromatic core, by means of the Wimperis pulse sequence. The spectral densities obtained from the measured relaxation times are discussed in terms of internal and overall molecular motions. A small step rotational diffusion model for the overall molecular motions, superimposed on a free rotational model for internal motions, allowed diffusion coefficients for molecular spinning and tumbling and for phenyl ring rotations to be derived for **HL**; the same models were used in describing the dynamics of **Azpac**.

Key words: Liquid Crystals; Deuterium Relaxation; Molecular Dynamics; Metallomesogens; NMR.

Introduction

Metal containing liquid crystals, known as *metallomesogens* [1], constitute a class of compounds of great interest because of their possible technical applications. However, because of the high transition temperatures, poor thermal stability and high viscosity usually exhibited by these compounds, few thorough characterisation studies are reported in the literature. Among these compounds, **Azpac** [2], the acetylacetonate derivative of the cyclopalladated 4,4′-bis(hexyloxy)azoxybenzene (**HL**), is exceptional having a low temperature nematic phase and good thermal stability; therefore it has been extensively investigated, and refractive indices, elastic constants, viscosity coefficients, dielectric permittivities and flexoelectric coefficients have been determined [3].

A quite detailed ^{2}H NMR investigation of orientational ordering and structure of **Azpac** has been recently performed by us [4]; a preliminary study of the dynamic behaviour of **Azpac** will be presented here and compared with that of the pure mesogenic ligand **HL**. To the best of our knowledge, this is the first NMR study of molecular dynamics on metallomesogens.

In recent years many NMR studies of liquid crystal molecules in mesophases have been performed using deuterons as spin probes to measure both the Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) spin-lattice relaxation times, allowing the spectral densities J_1 and J_2 to be determined. These spectral densities have been interpreted within motional models which assume a rotational diffusion mechanism for the molecular reorientational motion and allow for superimposed contributions [5] of order director fluctuations and internal motions. A number of models of increasing complexity has been proposed for describing the rotational diffusion of uniaxial molecules in uniaxial and biaxial phases as well as of biaxial molecules in uniaxial phases [6–9]. However, given the limited number of experimental data usually available, in most cases simplifying assumptions have been made, and the small step rotational diffusion model, proposed by Nordio and co-workers [6] for cylindrical molecules in uniaxial phases has been used.

In the present study the Nordio model, superimposed to free rotation of the phenyl rings about their *para* axes, has been applied in the interpretation of the

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spectral densities of **HL** and **Azpac**. Remarkable differences in the dynamics of the two compounds have been singled out: whereas **HL** can be considered to behave as a "normal" calamitic nematogen, in **Azpac** the molecular dynamics falls in a slow motional regime. In the latter case the validity of the Nordio model and, more generally, of diffusional models is questioned.

Experimental

The samples (Fig. 1) were available from a previous study [4], synthesized as described in [2, 10, 11].

Deuterium NMR experiments were performed at 46.04 MHz on a Bruker AMX-300 spectrometer equipped with a 4-mm CP-MAS probe; samples were enclosed in a sealed pyrex insert within a MAS ZrO_2 rotor. The 90-degree pulse was 4.6 μs. Temperature was controlled within 0.1 °C; the sole bearing air was used in order to avoid spinning of the sample.

^{2}H Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) spin-lattice relaxation times were measured by the Wimperis pulse sequence [12] $(90_0-2\tau_1-67.5_{270}-2\tau_1-45_{90}-\tau_1-45_{90}-\tau_2-45_0)$, with $\tau_1=24$ μs for **HL-d_4** and $\tau_1=22$ μs for **Azpac-d_4** and **Azpac-d_{26}**, experimentally optimised. This sequence allows simultaneous measurements of T_{1Z} and T_{1Q} for all different types of deuterons present in the sample. In fact, the intensity of the two peaks of a quadrupolar doublet changes as a function of τ_2 in such a way that the sum and difference of the two intensities are related to the relaxation times by

$$M_+(\tau_2)=2K\sin\alpha(1-e^{-\tau_2/T_{1Z}}) \tag{1 a}$$

and

$$M_-(\tau_2)=3K\sin\alpha\cos\alpha\, e^{-\tau_2/T_{1Q}}, \tag{1 b}$$

respectively [13], where α is the flip angle of the monitoring pulse, which has been chosen equal to 45°. The spectra of **HL-d_4** and **Azpac-d_4** were recorded under proton decoupling conditions. In all cases a relaxation delay of 4 s was used in order to allow the complete relaxation of the spin system and to avoid heating due to proton irradiation. Spectra with a good signal-to-noise ratio were obtained after 200 scans.

Theory

Using the standard spin relaxation theory for deuterons, the relaxation times T_{1Z} and T_{1Q} are related to the spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$ by

$$\frac{1}{T_{1Z}}=J_1(\omega_0)+4J_2(2\omega_0), \tag{2 a}$$

$$\frac{1}{T_{1Q}}=3J_1(\omega_0), \tag{2 b}$$

where ω_0 is the Larmor frequency.

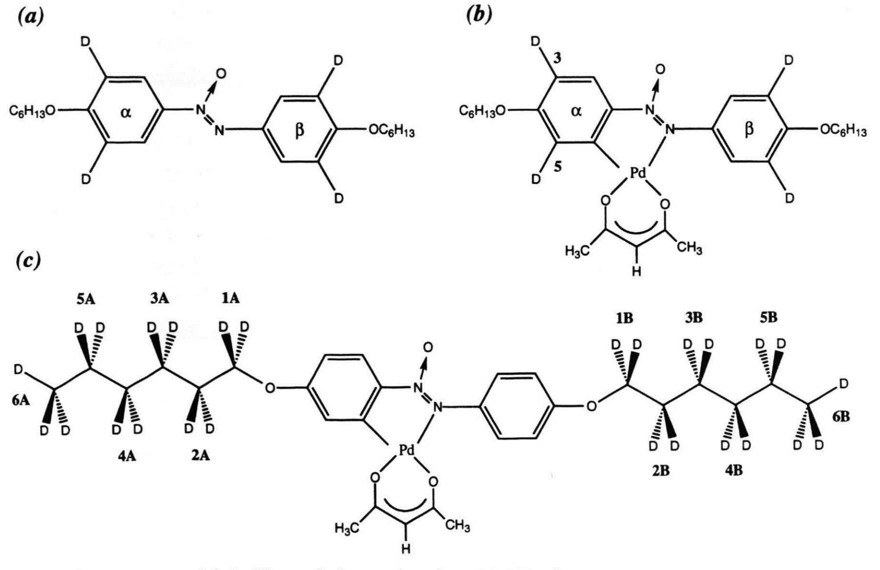

Fig. 1. Structure and labelling of the molecules: (a) **HL-d_4**; (b) **Azpac-d_4**; (c) **Azpac-d_{26}**.

Even though spectral densities contain all the dynamic information, it is necessary to express them in terms of more easily-handled quantities in order to discriminate the contributions of different motions. In fact, the complex dynamics of liquid crystals is characterised by the combined effect of three types of motions: collective motions such as order director fluctuations, reorientations of the whole molecule, and internal rotations and jumps.

A simplified theory [14, 15], which assumes that the order director fluctuations are small and not coupled to reorientational motions, predicts that, whereas $J_2(2\omega_0)$ is unaffected by this motion, its contribution to $J_1(\omega_0)$ in nematic phases has a characteristic $\omega_0^{-1/2}$ frequency dependence and therefore can be revealed by measuring relaxation times at different Larmor frequencies. This contribution can be written as

$$J_1^{\mathrm{DF}}(\omega_0) = \frac{A_{\mathrm{DF}}}{\sqrt{\omega_0}}, \tag{3}$$

where the proportionality factor A_{DF} depends on macroscopic parameters (order parameter, average Frank elastic constant, viscosity coefficient and autodiffusion translational constant) as well as on microscopic parameters related to the molecular geometry and the orientation of the C–D bonds with respect to the principal axis system, which contain second-rank Legendre polynomials. In particular, for aromatic deuterons in calamitic mesogens, the C–D bond forms angles close to the magic angle (54.7°) with respect to the symmetry axes relative to internal or molecular motions, giving rise to negligible contributions of the order director fluctuations to $J_1(\omega_0)$ [16, 17].

The reorientation of cylindrical molecules in uniaxial phases can be treated as small step rotational diffusion in the presence of an ordering potential, as in the model proposed by Nordio and co-workers [6]. In this model, the motion is described by a diffusion tensor diagonal in a molecular fixed frame, whose principal components, $D_{/\!/}$ and $D_\perp$, are the rotational diffusion coefficients of the molecule about the long axis and of the long axis, respectively. The spectral densities are calculated as the Fourier transforms of the autocorrelation functions, which can be written as a sum of decreasing exponential functions [7].

For deuterons which are fixed with respect to the molecular frame, the spectral densities are related to the diffusion coefficients by

$$J_{m_L}^{fix}(m_L\omega_0) = \frac{3\pi^2}{2}(\nu_q)^2 \sum_{m_M=-2}^{2} c_{m_L m_M}\,[d^2_{m_M 0}(\beta_{M,Q_0})]^2 \cdot \sum_j a^{(j)}_{m_L m_M} \frac{(\tau^{(j)}_{m_L m_M})^{-1}}{(m_L\omega_0)^2 + (\tau^{(j)}_{m_L m_M})^{-2}}, \tag{4}$$

where ν_q is the quadrupolar coupling constant, d^2_{rs} are the reduced Wigner matrices, β_{M,Q_0} is the angle between the molecular long axis and the C–D bond of interest, $a^{(j)}_{m_L m_M}$ represent normalised relative weights of each exponential function with time constant $\tau^{(j)}_{m_L m_M}$, $c_{m_L m_M}$ are the initial amplitudes of the correlation functions, and the correlation times $\tau^{(j)}_{m_L m_M}$ are defined as

$$\frac{1}{\tau^{(j)}_{m_L m_M}} = \frac{6D_\perp}{b^{(j)}_{m_L m_M}} + m_M^2(D_{/\!/} - D_\perp). \tag{5}$$

The coefficients $a^{(j)}_{m_L m_M}$, $b^{(j)}_{m_L m_M}$, and $c_{m_L m_M}$ depend on the principal order parameter and are tabulated in [7] for a Maier-Saupe potential.

Internal motions are usually considered decoupled from the overall reorientation of molecules and then described by a suitable superimposed model. While for aliphatic chains, models taking into account conformational distributions are requested, the rotation of phenyl rings about their *para* axes can be treated as free rotational diffusion [5]; in this case the spectral densities can be written as

$$J_{m_L}^{rot}(m_L\omega_0) = \frac{3\pi^2}{2}(\nu_q)^2 \sum_{m_M, m_R=-2}^{2} c_{m_L m_M} \cdot [d^2_{m_R 0}(\beta_{R,Q_R})]^2\,[d^2_{m_M m_R}(\beta_{M,R})]^2 \cdot \sum_j a^{(j)}_{m_L m_M} \frac{(\tau^{(j)}_{m_L m_M})^{-1} + \xi(m_R)\,D_R}{(m_L\omega_0)^2 + [(\tau^{(j)}_{m_L m_M})^{-1} + \xi(m_R)\,D_R]^2}, \tag{6}$$

where D_R is the diffusion coefficient relative to the internal rotation of the phenyl ring, β_{R,Q_R} is the angle between the C–D bond and the *para* axis of the phenyl ring, while $\beta_{M,R}$ is the angle between this axis and the molecular long axis; $\xi(m_R)$ is $(1-\delta_{m_R})$ or m_R^2, if the strong collision [18] or small step diffusion [19] models are used, respectively.

Results and Discussion

Assignment of ^2H Spectra

HL. The proton-decoupled deuterium spectra of **HL-d_4** (Fig. 2a) show two pairs of quadrupolar dou-

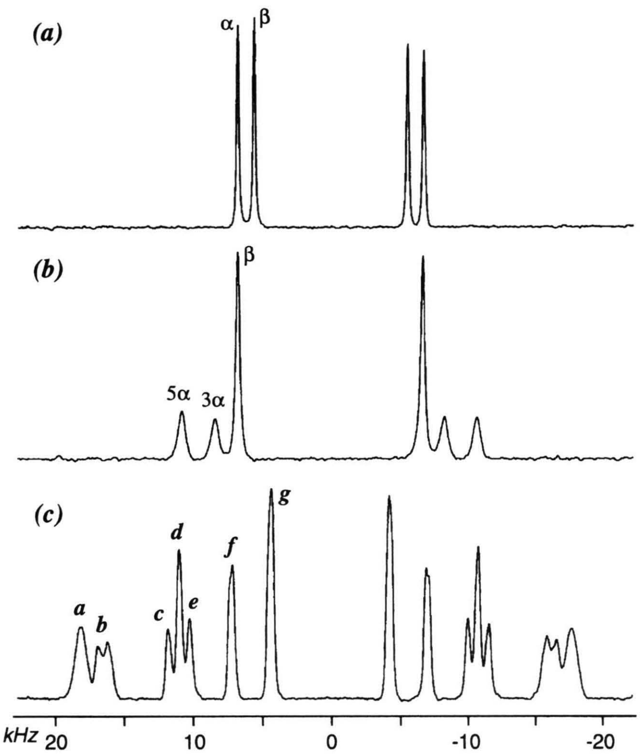

Fig. 2. ^{2}H NMR spectra of: (a) **HL-**d_4 at 383 K; (b) **Azpac-**d_4 at 369 K; (c) **Azpac-**d_{26} at 369 K; spectra (a) and (b) are recorded under proton decoupling conditions.

blets, each corresponding to the deuterons of a phenyl ring. On the basis of a previous orientational order study [4], the inner doublet is ascribable to deuterons on ring β and the outer one to deuterons on ring α.

Azpac. The ^{2}H spectra of **Azpac-**d_4, recorded under proton decoupling conditions (Fig. 2b), consist of three pairs of quadrupolar doublets: as described in [4], the outer pairs of equal integrated intensity are assigned to deuterons **3**α and **5**α, while the inner pair, with double intensity, is due to both deuterons on ring β, undergoing fast rotation around its *para* axis.

The quadrupolar splittings measured at each temperature for **HL-**d_4 and **Azpac-**d_4 were in complete agreement with the values reported in [4]. By taking into account the findings of the previous work, concerning the molecular geometry and the location of the principal axes system, the quadrupolar splittings have been used to calculate the order parameters to be included in the dynamic investigation.

In the ^{2}H NMR spectra of **Azpac-**d_{26} (Fig. 2c) eight pairs of doublets are distinguishable, whose quadrupolar splittings increase with decreasing temperature (see Figure 3). The assignment is rendered difficult both by the presence of two non-equivalent chains in the molecule, and the absence of a general rule to discriminate signals arising from a single chain. It is often assumed that the quadrupolar splittings should decrease monotonically along an alkyl chain, going from the phenyl ring towards the methyl group, however this is not strictly valid. In fact, selective deuteriation of several mesogens and, in particular, of the members of the series of the 4,4′-bis(alkoxy)azoxybenzenes with seven and eight carbon atoms in the chains [20], has shown that an alternation in magnitude of the quadrupolar splittings could be present for deuterons at positions 3 and 4. On this basis, the deuterium spectra of **Azpac-**d_{26} were partially assigned in our previous work [4], with uncertainties regarding positions 3 and 4. A relaxation investigation on deuterons in the chains is helpful in this regard, since in all cases studied [18, 21] spin-lattice relaxation times were found to increase monotonically along the chains, reaching the maximum value for the methyl group. Even though in our case it is not possible to discriminate between the signals belonging to the two different chains, a measurement of relaxation times allowed the assignment of all the signals, and particularly of those relative to the methylene groups 3 and 4. In fact,

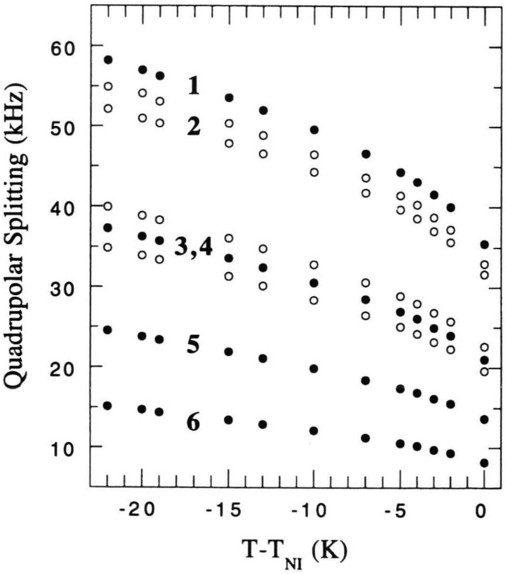

Fig. 3. Quadrupolar splittings of the different deuterons of **Azpac-**d_{26} vs. $T-T_{NI}$, T_{NI} being the nematic-isotropic temperature transition.

at each temperature both T_{1Z} and T_{1Q} obtained for the different quadrupolar doublets by means of the Wimperis sequence obey the relationship

$$T_1(\boldsymbol{a}) < T_1(\boldsymbol{b}) < T_1(\boldsymbol{e}) < T_1(\boldsymbol{d}) < T_1(\boldsymbol{c}) < T_1(\boldsymbol{f}) < T_1(\boldsymbol{g}),$$

leading to the assignment reported in Table 1. It must be pointed out that the relaxation times measured are not the individual values for each deuteron type, with the exception of $T_1(\boldsymbol{e})$ and $T_1(\boldsymbol{c})$ corresponding to deuterons 3 and 4 of different chains, respectively; $T_1(\boldsymbol{a})$, $T_1(\boldsymbol{b})$, $T_1(\boldsymbol{f})$ and $T_1(\boldsymbol{g})$ are in fact an average between the values relative to corresponding deuterons in the two different chains, while $T_1(\boldsymbol{d})$ is an average value between the relaxation times of deuterons 3 and 4 of different chains. As an example, the relaxation times determined at 362.5 K are shown in Fig. 4a as functions of the position in the chain.

On the basis of the assignment just performed, an inversion between deuterons in positions 3 and 4 in the trend of the quadrupolar splittings can be noticed (see Figure 4b).

Dynamics

HL. The spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$ calculated from the relaxation times (see (2a–b)) for deuterons on rings α and β of **HL**-d_4 are reported in Figure 5. All the spectral densities increase regularly with lowering the temperature in the nematic phase, the J_1/J_2 ratio going from 1.7 to 2.4, as usually found for aromatic deuterons in calamitic nematogens ([17], see also Table 5.1 of [5]).

The experimental spectral densities were interpreted using the Nordio model superimposed to a free rotational diffusion model in the strong collision limit for the rotation of phenyl rings α and β about their *para* axes, as described previously. In order to obtain the diffusion coefficients of both overall ($D_{//}$ and $D_\perp$) and internal ($D_{R\alpha}$ and $D_{R\beta}$) molecular motions (5) and (6) were employed with the following assumptions: the quadrupolar coupling constant is 185 kHz, the angle β_{R,Q_R} is 60°, the principal molecular axis lies along the *para* axis of ring α and the angle between the *para* axes of the two phenyl rings is 9.5°, according to the find-

Table 1. Assignment of the deuterium spectrum of **Azpac**-d_{26}. Peak labels and deuterium positions refer to Figs. 2c and 1c, respectively.

Peak	Deuterium position
a	1A, 1B
b	2A, 2B
c	4A (4B)
d	3A (3B), 4B (4A)
e	3B (3A)
f	5A, 5B
g	6A, 6B

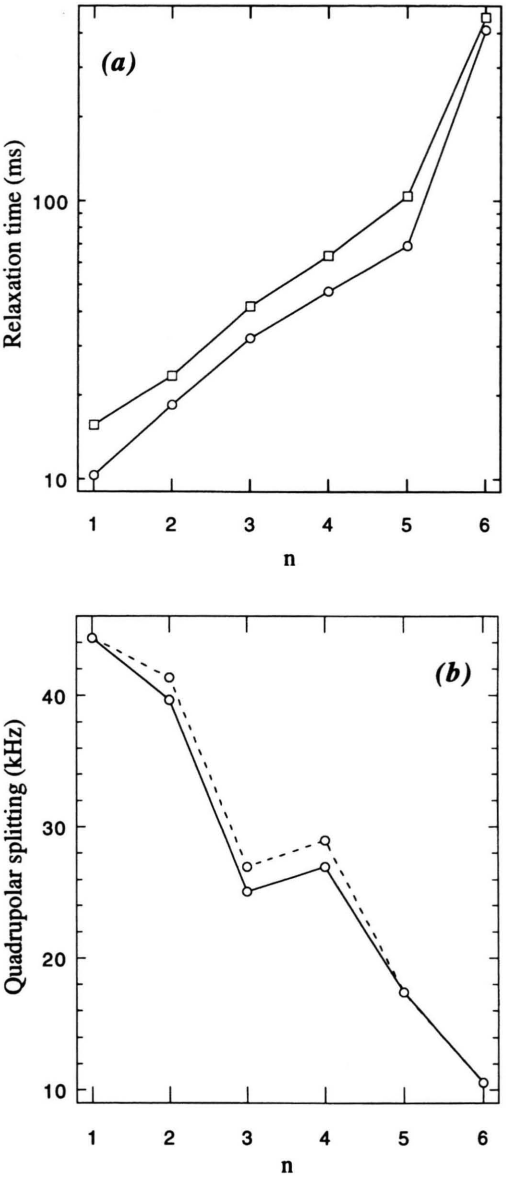

Fig. 4. (a) Spin-lattice relaxation times T_{1Z} (circles) and T_{1Q} (squares), and (b) quadrupolar splittings of deuterons of **Azpac**-d_{26} as functions of the position in the alkoxy chains at 369 K. In (a) the reported values for $n = 3$ and 4 refer to peaks ***e*** and ***c***, respectively.

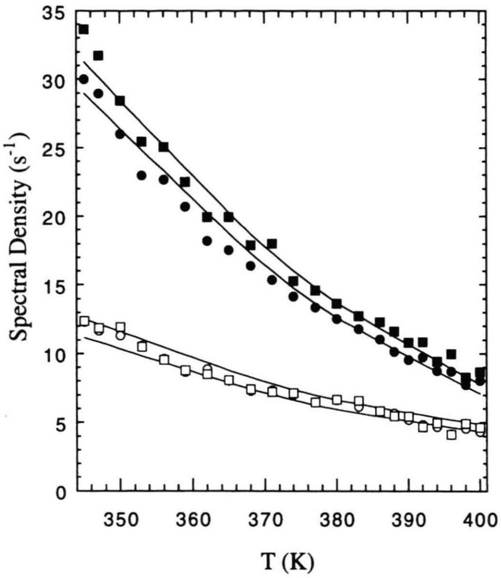

Fig. 5. Experimental spectral densities $J_1(\omega_0)$ (filled symbols) and $J_2(2\omega_0)$ (open symbols) of **HL-d_4** in the nematic phase vs. temperature. Circles and squares refer to α and β aromatic deuterons, respectively. Errors are within 5%. Spectral densities resulting from the fitting procedure reported in the text are represented by solid lines.

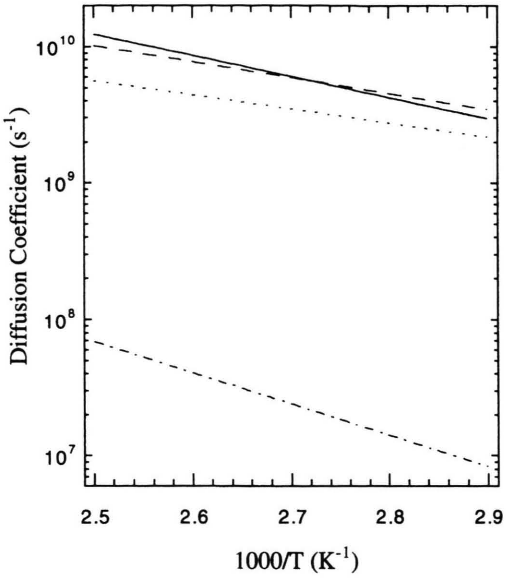

Fig. 6. Diffusion coefficients $D_{//}$ (solid line), $D_\perp$ (dot-dashed line), $D_{R\alpha}$ (dashed line) and $D_{R\beta}$ (dotted line) of **HL-d_4** in the nematic phase vs. reciprocal temperature.

ings of [4]. Good results were obtained (see Fig. 6) applying a non-linear global least-squares fitting procedure to the experimental data, assuming an Arrhenius temperature dependence for the diffusion coefficients. The spinning overall motion and the internal rotation of the aromatic rings are clearly the predominant dynamic processes, their diffusion coefficients ($D_{//}$, $D_{R\alpha}$ and $D_{R\beta}$) being two orders of magnitude higher than that describing the molecular tumbling ($D_\perp$), with $D_{R\alpha}$ slightly higher than $D_{R\beta}$. The latter observation follows what previously found in the only deuterium relaxation study present in the literature where two different aromatic rings of a calamitic mesogen (i.e. 4,4′-bis(heptyl)azoxybenzene) have been investigated [17]: in both cases the rotation of the ring closest to the N–O group is faster. Activation energy values of 29.7, 43.9, 22.4 and 19.9 kJ mol^{-1} were found for $D_{//}$, $D_\perp$, $D_{R\alpha}$ and $D_{R\beta}$, respectively, indicating that the tumbling molecular motion is the most hindered dynamic process.

Azpac. Relaxation time measurements have been performed at different temperatures within the nematic range of **Azpac-d_4**, allowing T_{1Z} and T_{1Q} and consequently $J_1(\omega_0)$ and $J_2(2\omega_0)$ for all deuterons to be obtained (see Figure 7). Apart from the two highest

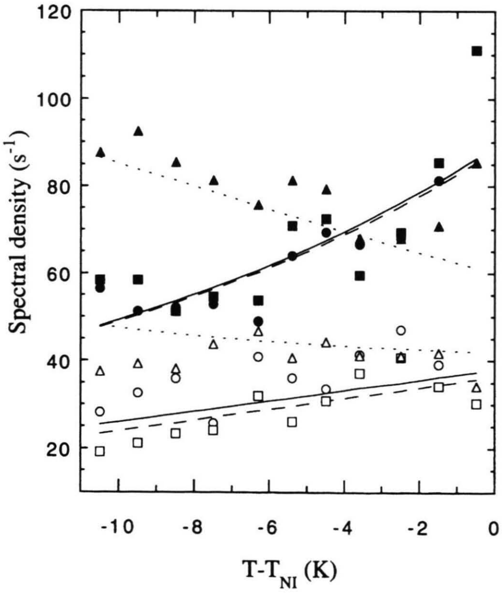

Fig. 7. Experimental spectral densities $J_1(\omega_0)$ (filled symbols) and $J_2(2\omega_0)$ (open symbols) of **Azpac-d_4** in the nematic phase vs. $T-T_{NI}$. The lines are results of the least-squares global fitting described in the text. Circles and solid lines, squares and dashed lines, triangles and short dashed lines refer to **5**α, **3**α, and β aromatic deuterons, respectively. Experimental errors are within 15%.

temperatures, deuterons on ring β show an increasing trend of $J_1(\omega_0)$ with lowering the temperature, as usually observed, whereas $J_2(2\omega_0)$ remains almost constant, giving rise to a growing J_1/J_2 ratio. On the contrary, deuterons on ring α show a different behaviour with both $J_1(\omega_0)$ and $J_2(2\omega_0)$ decreasing with lowering the temperature. The apparently anomalous trend of these spectral densities, which depend only on overall molecular motions, is actually expected on the basis of (4) in the slow motion region ($\omega_0 \tau^{(j)} > 1$). The different trend of spectral densities of deuterons on ring β is to be ascribed, on the basis of (6), to the internal rotation of the ring about its *para* axis, which should be predominant and in the fast motion regime.

A non-linear least-squares global fitting of the experimental spectral densities of all deuterons at all temperatures, performed using the Nordio model with a superimposed free rotation for ring β, confirmed these observations. Satisfactory results (see Fig. 7) could be obtained only assuming a small step model for the internal motion; the corresponding diffusion coefficient was found to obey the Arrhenius equation $D_R = 1.2 \times 10^{13}$ $\exp(-27.8/RT)\,\mathrm{s}^{-1}$, where R is in kJ mol^{-1} K^{-1}. As far as the diffusion coefficients for the overall molecular motions, $D_{/\!/}$ and $D_\perp$, are concerned, only their order of magnitude ($D_{/\!/} \approx 10^5 \div 10^6\ \mathrm{s}^{-1}$ and $D_\perp \approx 10^3\ \mathrm{s}^{-1}$) could be determined because of the strong correlation between the parameters involved in the fitting, and the relatively large experimental error of the spectral densities, combined with the quite small temperature range investigated. The low values of the molecular diffusion coefficients seem reasonable, considering the high average viscosity observed for **Azpac** [3]. A better fitting could probably be obtained using the more suitable model proposed by Tarroni and Zannoni [8] in order to describe reorientation of asymmetric molecules in uniaxial phases, given the non-negligible molecular biaxiality of **Azpac**, also pointed out by the previous orientational order study [4]. Again, the molecular reorientation is described as small-step rotational diffusion, but a biaxial restoring potential is assumed and the diffusion tensor is written in terms of D_z for the spinning motion and two different diffusion coefficients, D_x and D_y, for the tumbling motion, thus overcoming the assumption $D_x = D_y = D_\perp$.

It must be pointed out, however, that these diffusional models may not be valid in the slow molecular motion regime; in fact, when the restoring potential cannot be considered time independent any longer, more complicated approaches must be used [22, 23]. Vold and Huo [24] have treated the case of a solute in a liquid crystalline solvent in the intermediate and slow motion region in a heuristic way, introducing a

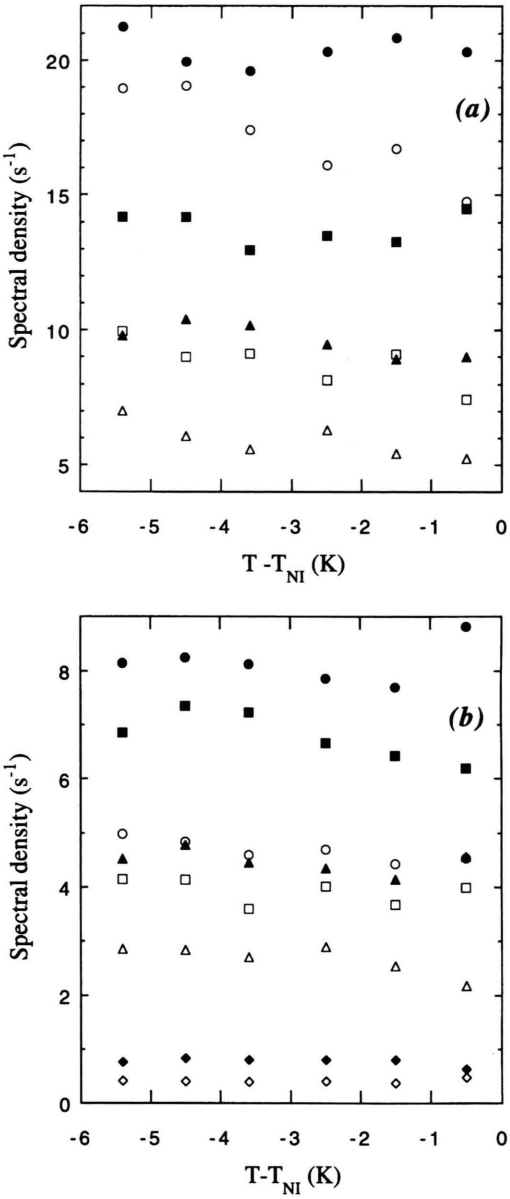

Fig. 8. Experimental spectral densities $J_1(\omega_0)$ (filled symbols) and $J_2(2\omega_0)$ (open symbols) of **Azpac-d_{26}** in the nematic phase vs. $T - T_{NI}$. In (a) circles, squares and triangles refer to peaks ***a***, ***b*** and ***e***, respectively; in (b) circles, squares, triangles and diamonds refer to peaks ***d***, ***c***, ***f*** and ***g***, respectively. Experimental errors are within 10%.

parameter which corrects the Debye spectral densities for a fluctuating potential, following Polnaszek et al. [25]. The application of a similar approach to the spectral densities of **Azpac** did not improve the fitting for acceptable values of the correction parameter [26]. This indicates that, in order to obtain more detailed information on the dynamics, more complex models must be used, which require, moreover, a larger set of experimental data, and in particular spectral densities at different frequencies allowing frequency dependent dynamic processes to be monitored.

As anticipated in the previous section, relaxation time measurements have also been performed in the nematic phase of **Azpac-d_{26}**; the corresponding spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$ are reported in Figure 8a–b. All spectral densities show a practically constant or slightly increasing trend with lowering the temperature. This suggests that the predominant relaxation mechanism is the internal rotation about C–C bonds in the chains. A detailed analysis of these data is currently in progress.

Conclusions

The relaxation data measured for **HL** can be successfully modelled assuming small step rotational diffusion for the overall molecular reorientation and free rotation in the strong collision limit for the two aromatic rings. The diffusion coefficients obtained take up values in the range usually found in nematic phases and show that the spinning motion is faster than the tumbling motion, the latter being the most thermally activated process. The two rings show a similar dynamic behaviour, the two internal rotational diffusion coefficients being slightly different but equally activated.

The cyclopalladation of **HL**, besides sensibly increasing the molecular biaxiality, has dramatic effects on the dynamics: the molecular diffusion coefficients obtained for **Azpac**, applying the same model, are sensibly lower with respect to those of **HL** and to those usually found in nematic phases, and the internal rotation of the non-coordinated ring results to be in the small step diffusion limit. Although the model used is too simplifying, the diffusion coefficients obtained are reasonable considering the high viscosity determined for **Azpac**.

The relaxation times of the chain deuterons allowed the assignment of the spectra of **Azpac-d_{26}**; no detailed dynamic models were applied in this case, however the data indicate that the internal motion is the dominant process for relaxation.

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