Chapter 6

Field Cycling NMR Studies of Molecular Dynamics in Butyloxy Benzylidene Alkylanilines (4O.m)

Chapter 6 deals with the study of the relationship between end chain structure and molecular dynamics in the homologous series, Butyloxybenzylidene Alkylanilines (40 m). These systems belong to the well known, nO.m series of Liquid crystals. The chapter consists of 9 sections.

Section 6.1: Motivation and objectives of the present study are described towards the beginning of the section. Earlier structure-property studies on nO.m systems as well as NMRD studies on other homologous series of systems are reviewed next. Experimental details and the models followed in the NMRD data analysis in terms of different contributions (DF, SD, R and LU) to the total relaxation rate are also presented.

Sections 6.2 to 6.8: Experimental data obtained from different liquid crystalline systems (40.2, 40.3, 40.4, 40.5, 40.7, 40.8 and 40.9) of the 4O.m series are presented in these sections. These systems are treated independently and the results obtained from the NMRD data analysis are presented separately for different phases. Dynamic parameters obtained from the analysis are presented in tables for each system and phase.

Section 6.9 Structure-Dynamics relationships obtained from the present study are presented in this concluding section. Different dynamic parameters obtained as a function of end chain properties are compared and plotted independently. Relative contributions of the three important dynamics (DF, SD and R) are plotted as a function of chain length at different frequencies.
6.1. Earlier studies and present objectives of molecular dynamics in Liquid Crystals

6.1.1. Introduction

The systems under the present NMRD study belong to the well known N(p-n-alkoxybenzylidene) p-n-alkylaniline homologous series (nO.m series), which have two terminal chains, where *n* is the number of carbon atoms in the alkoxy end chain and *m* is the number of carbon atoms in the alkyl end chain. This homologous series (nO.m) has the molecular structure depicted in the scheme given in figure 6.1.

![Figure 6.1. General molecular structure of the nO.m homologous series of systems.](image)

The present NMRD studies are carried out on the systems, 40.2, 40.3, 40.4, 40.5, 40.7, 40.8 and 40.9, i.e., keeping *n* = 4 as constant in the above molecular structure and changing the alkyl chain length, by choosing systems having *m* from 2 to 9. This series exhibits a series of smectic (S\textsubscript{A}, S\textsubscript{C}, Se, and S\textsubscript{G}) phases and a nematic phase with variable stabilities. The present experimental work includes frequency dependent proton *T\textsubscript{1}* study (NMRD) using FCNMR technique in different phases of these systems. Earlier work done in this laboratory [1,2] using conventional NMR techniques (*T\textsubscript{1}, T\textsubscript{JD}* ) is also used in the analysis in order to get the complete picture of molecular dynamical parameters. Temperature dependent data are available at high frequencies (4 to 50 MHz) on these (40.2, 40.3, 40.4, 40.5, 40.7, 40.9) systems. Phase sequences of the 40.m systems are shown in figure 6.2.

6.1.2. Motivation and objectives

The homologous series nO.m of systems are chosen, keeping the following reasons and expectations in mind. Some of the reasons listed below are general in nature to any molecular dynamics study of liquid crystals.
Figure 6.2  Phase sequences of the 4O.m systems. The temperature range of the nematic phase for each system is shown with the shaded area 1). This homologous series (nO.m) have been studied extensively, using all possible techniques, by various groups [6] in order to elucidate the microscopic structure and its relationship to the macroscopic physical properties. For example, the most studied MBBA (10 4), using almost all the physical techniques, including NMRD studies [3,4] belongs to this nO.m series. Using the vast amount of data on structural and physical properties available, it is expected to be easier to explain the more complex, microscopic molecular dynamics in these homologous systems. They have rich polymorphism and have convenient temperature regions to work with. The transition
temperatures of different mesogens were measured [5] using calorimetry and optical microscopy, by varying \(n\) from 1 to 7 and \(m\) from 4 to 8, which are verified later by other studies also. Databases are also available on some of these systems [6].

2) In particular, the 40.m series, has a special significance because it shows very stable nematic phases over a wide temperature region, and very easily accessible for experimentation. These systems exhibit nematic phases having temperatures from 45.2°C (40.4) to 83°C (40.7) and the nematic temperature range varies from about 39°C (40.5) to 8°C (40.12). Such a broad variation in the nematic phase temperature range and transition temperatures in this series is not only useful but also convenient for temperature dependent studies. These systems exhibit increasing smectic A phase stability when the chain length is gradually increased.

3) The controversy over the nature of the nematic-smectic A transition, is another important reason to study, since these systems exhibit continuously differing N-S\(_A\) transition order. In 40.m liquid crystals, this particular transition shows a second order, and a weakly first order nature depends on the chain length of the molecules, which were different from the theoretical predictions. The refractive index and density studies carried out by Potukuchi [7] have demonstrated the presence of a tricritical point for nematic-smectic A transition and also has shown that the McMillan parameter for the nO. m homologous series is different from the other results for other series of liquid crystals. The order of the nematic to smectic A transition has shown different behaviors. A first order transition is observed in 60.4, 60.8, 70.1, and 70.4 systems. A weakly first order transition is observed in 50.8 and a second order phase transition in 40.4, 40.6, 40.7, 40.8 and 40.10 systems. These observations suggest that alkoxy end chain play an important role in this transition. These observations highlight the importance of these systems and the molecular level dynamical properties would be more useful to understand this behavior.

A variety of pretransitional effects in the nematic phase near the second order nematic-smectic A transition result from the thermally excited fluctuations in the smectic order. The smectic A density correlated over a relatively short range (called cybotactic clusters) appears and decays away. de Gennes [8] has suggested that the
N-SA transition should be identical to the superfluid-normal transition. It was disputed by Halperin et al., [9], who have argued that it should be similar to the superconductor-normal transition with director fluctuations (DF) driving the transition to the first order. The influence of the coupling between the orientational order and translational order on the order of the N-SA transition was studied by Longa [10].

Contrary to the first order nature seen in the nCB, nS5 homologous series and other systems and mixtures with short nematic temperature ranges, the nO.m homologous series of systems showed a first order, second order and weakly first order transitions. Since it is possible to get information on director fluctuation from NMRD studies, the systematic study on these systems, would be useful to understand molecular dynamic processes responsible for such phase transitions.

4). A variation of the end chain length from \( m = 2 \) to \( m = 9 \), gives an opportunity to probe dynamics of different nematic phases and compare the results in terms of the usually observed odd-even effects, chain length effects and symmetry effects as explained below.

a) Odd-odd systems (40.3, 40.5, 40.7 and 40.9) and odd-even systems (40.2, 40.4 and 40.8) which could give information about the famous 'odd-even effects' in dynamics, which were already shown by Noack et al., [4] and Dong et al., [11] in liquid crystals. It is well known that odd-even effects are seen in almost all macroscopic physical properties studied in liquid crystals.

b) It is also known that the chain length alters the phase stabilities of the nematic and smectic phases. This homologous series provides an opportunity to study shorter (40.2, 40.3) and longer (40.8 and 40.9) chain systems, within the odd or even systems.

c) There is another property that can be taken seriously, based on the existing experimental data, though it is not frequently mentioned in the literature on liquid crystals i.e., 'balancing of the terminal chains' or "symmetric and non-symmetric end chains". The effect of symmetry on the nematic phase stability in 4O.m systems is presented in chapter-4. Transition energies as well as transition entropies [5] of these systems seem to show a kind of symmetry effects as shown in figure 6.3.
Figure 6.3. Isotropic-nematic transition entropies (a) and transition energies (b) for the nO.m homologous series. Systems having symmetric end chains show a pronounced difference when comparing the immediate neighbors of the same series. The data are taken from the literature [5].
The general trend in these figures seems to show either a peak or a deviation when the end chains are close to balanced. The present family of the systems gives an opportunity to study molecular dynamics of balanced-odd (40.5) and balanced-even (40.4) systems, without changing the molecular length too much. It is known that the longer chain smectic systems showed conformational jumps and hence the orientational disorder in these systems. Cybotactic clusters were seen above N-S\texttext{A} transition in longer chain systems.

Moreover, no systematic NMRD studies over wide frequency range were done on this particular family (40 m) so far. There exist some experimental efforts by this group, using the conventional NMR technique [1,2] and by others [12] using the deuterium NMR relaxation time measurements on this series. There has been no attempt to see the low frequency spectral densities, which could give direct information about the connection between phase stabilities and collective director fluctuations on this homologous series.

Since collective motions are superimposed on simultaneous non-collective rotations and translational reorientations of individual molecules, a clear distinction of these, require a very wide nematic range NMRD studies. It has been established that these collective motions dominate at a low kHz regime and that individual motions dominate at conventional high frequencies. The available data is insufficient for an understanding of the molecular level microscopic behavior, and also in correlating the rich theoretical understanding on liquid crystal physics.

There is no clear understanding of the three dynamical properties (DF, SD, R) on the end chain structure, as yet. It has been reported that [13], near the I-N transition, rotations about the short axis is an important mechanism in mediating the spin relaxation. The low temperature nematic, close to N-S\texttext{A} transition is dominated by DF and SD mechanisms, where rotations contributes lesser. A systematic study at the high temperatures closer to the I-N transition sufficiently away from the region where pre-transitional effects dominate the spin relaxation, are to be useful means of separating the R, about the short axis from the collective DF modes.
The DF contribution and the value of the constant \( \text{(ADF)} \) in nematic liquid crystals are considered to be important factors. Procuring some information on the cut-off frequencies is also important. With the available computational facilities it has been possible to implement model fitting with very many parameters. The modifications introduced by Blinc [14], Doane and Johnson [15], Vold and Vold [16] and several others, to the basic model proposed by Pincus et al., [17] lead to a more generalized model [18]. Model fitting for the DF contribution can be done using these models. The anisotropic elastic constants model could be implemented if the experimental elastic constants are available for the system.

In the present series, the experimental data available on 40.4 [30] has made such an attempt possible. The differences between the one constant approximation model and the anisotropic elastic constants model in implementing them, for the NMRD data would be interesting. Introduction of upper as well as lower cut-off frequencies makes DF contributions more meaningful. NMRD studies on PAA [49] have shown a decreasing \( \text{ADF} \) value with an increasing chain length. There are nevertheless, observation [12] in the literature that the \( A_{DF} \) decreases with chain length, in homologous series.

### 6.1.3 Review of earlier studies on nO.m compounds

Experimental attempts on different homologous series were carried out by various groups with typical objectives such as, the effect of molecular structure on polymorphism and changes in the molecular parameters, as one runs through the homologous series. There have been attempts to look for the physical systems to test the validity of theoretical models built, to explain static/dynamic features of liquid crystals. Optical microscopy, miscibility, and X-ray diffraction methods were used by Goodby et al., [19], for studying different homologous of nO. m series.

Pisipati and coworkers [7] have studied the nO.m series of systems using thermal microscopy, density, ultrasonic velocity, refractive index, magnetic resonance, DSC, and the XRD techniques. There are a number of publications [7] on
these studies. The static physical properties of all the available possible phases in this series had been studied, and various relevant physical properties and critical exponents were explained. The results showed that the 1-N, 1-S_A, N-S_C, N-S_G, S_C-S_C, S_H-S_G, and S_A-S_F phase transitions are of the first order phase transitions.

The SA-SC transition had showed a second order behavior in all the nO.m systems studied by Pisipati and coworkers [7]. The results from density, ultrasonic, X-ray, dielectric, ultrasonic relaxation, NMR, ESR, DSC, IR and refractive index studies on the system 40.4 had shown a first order I-N, S_A-S_B, and a second order N-S_A transition. 40.7 and 40.8 systems showed second order N-S_A, S_A-S_C transitions as observed from the calorimetric, light scattering and X-ray studies. ESR line width studies of 40.6 had shown the pretransitional effects near the N-S_A transitions. Density and ultrasonic studies had shown the weak first order nature of 40.12, and a second order nature on 40.10. The density and refractive index studies on 40m systems had been carried out by Potukuchi et al., [7].

Takahashi et al., [20] have studied variation of specific volume with temperature in the 50m series by changing m from 4 to 14. Neutron scattering experiments were used to study the co-operative nature of the molecular motions in S_H and S_o phases of 50.7 [21]. Limmer et al., [22] have performed line width measurements on three nO.m compounds 50.6, 70.5 and 70.6.

### 6.1.4. Earlier NMR relaxation measurements in Homologous series

Normally it is difficult to isolate the individual contributions (due to each dynamical mechanism) from a $T_1$ study of a narrow frequency range except for a few fortuitous cases. However, the earlier work on a few liquid crystal systems had reported the identification of different dynamical processes in a limited frequency range. It was shown particularly, that the frequency dependent studies of relaxation times combined with temperature dependent studies could be effectively used to obtain information about these mechanisms. There have been several studies on molecular dynamics through conventional NMR relaxation measurements in liquid crystals [1, 2, 12, 16, 23, 24, 25].
The FCNMR technique has been used to investigate molecular dynamics in liquid crystals by Noack and coworkers [11]. Proton spin relaxation studies on nematic homologs of PAA were carried out by Nagel et al., [26]. From these studies certain differences in dynamics were observed with the changes in the chain length. Shorter chain molecules (PAA) show higher values of $T_1$, than the longer chain molecules (PAB, HAB) at any particular nematic temperature. The DF contribution (quantified by the constant $A_{DF}$) varies with the chain length in the PAA series [27]. Longer chain molecules have a higher value of $A_{DF}$.

Another important conclusion arrived at, in the case of PAA and PAB studies is that, the chain protons also contribute to the value of the $A_{DF}$, contrary to the belief that, only the core involves in the collective fluctuations. This was also verified by a line shape analysis of these compounds [26]. The behavior of activation energies and upper cut-off frequencies obtained for the DF modes were used to support these conclusions. The decrease of the upper cut-off frequency with increasing chain length in PAA series ($8.1 \times 10^9 \, \text{s}^{-1}$ for PAA and PAA-d$_6$, $6.4 \times 10^9 \, \text{s}^{-1}$ for PAB, $1.1 \times 10^9 \, \text{s}^{-1}$ for HAB) suggests that the whole molecule undergoes DF dynamics. The square root region shifted with the chain length, in different systems studied [11] reveal that, longer the chain length of the molecule, longer the region having square root dependence.

It is generally observed from these studies that, due to the modulation of the inter-proton dipolar interaction, the proton spin-lattice relaxation times are sensitive to the following mechanisms.

1. **Director fluctuations** (DF) are dominant at very low frequencies (below few MHz) in the nematic phase with the usual square-root dependence on the proton Larmor frequency. It has weak temperature dependence. In the smectic A phase the DF mechanism is replaced by the smectic layer undulation modes (LU), which are generally described by a linear dependence with Larmor frequency.
2. The second mechanism, is the anisotropic translational \textit{self-diffusion} (SD), which is strongly temperature dependent, and generally dominates the high frequency relaxation from 10 MHz to a few 100 MHz in the \textbf{nematic phase}.

3. \textit{Rotations about the short axis} (R) dominate the intermediate frequency range. The R contribution is frequency independent, generally up to 1 MHz and frequency dependent, up to a few MHz. These rotations are generally observed in the \textbf{nematic} phase close to the I-N phase transition [13].

4. \textit{Reorientations about the long axis} and the ring flips were observed in the high frequency regime from a few tens of MHz to a few hundred MHz. Segmental rotations and conformational jumps have also been observed by many researchers [12] at high frequencies. These rotations are best studied, by the deuterium NMR methods and by angular dependent studies. There are various rotational models available, in the literature [12].

5. \textit{Order fluctuations} (OF) dominate the 1) value near the transitions. This has inverse temperature dependence.

6. Dipolar effects lead to a shallow region at low frequencies below 10 kHz.

7. The \textit{cross relaxation} process becomes effective when the dipolar proton splitting frequencies and the quadrupolar nitrogen transition frequencies overlap, allowing a resonant exchange between the two spin systems, thus shortening the relaxation time at special frequencies.

6.1.4.1. Earlier observations on Order and Director Fluctuations (OF and DF)

The orientationally ordered nematic liquid crystal phase is similar to the case of the Heisenberg ferromagnet and is a spontaneously broken continuous orientational symmetry of the high temperature isotropic phase [27]. As a consequence, the spectrum of collective fluctuations of the nematic director field is expected to be gapless in the long wavelength limit, and the so-called Goldstone mode should exist.
The spectrum of eigen modes of these excitations consists of one branch of propagating acoustic waves and of two pairs of over damped, non-propagating modes. These can be further separated into low and a high frequency branches. The branch of low frequency modes corresponds to a slow collective orientational relaxation of an elastically deformed nematic structure, whereas the fast modes correspond to over damped shear waves, which are similar to the shear wave modes in ordinary liquids. In the long wavelength limit, the relaxation rates for both the modes are proportional to $q^2$, which is characteristic of hydrodynamic modes. Here, $q$ is the wave-vector of the over damped mode.

In 1968, de Gennes [8] had introduced the concept of orientational normal modes, similar to the phonon collective excitations in 3D solids, which can be considered as plane, wave like, spatially coherent excitations of the director field $n(r, t)$. In contrast to the phonons in solids, collective modes in liquid crystals are always over-damped due to high viscosity. Soon after de Gennes suggestions, Blinc [14] and Pincus [17] showed the characteristic square root frequency behavior of $T_i$ in nematics and the failure of BPP theory of liquids in liquid crystals. This $T_i \propto \omega^2$ behavior ($\omega$ is the Larmor frequency) is a direct result of the gapless Goldstone mode nature, of the director fluctuations [27].

There have been attempts to study the pre-transitional dynamic behavior and order fluctuations (OF) near the I-N phase transition using the NMRD technique. NMRD studies by Wolfel et al., [28] on PAA and $T_i$ measurements by Dong et al., [29] on MBBA, showed a critical dependence of $T_i$ with frequency near phase transition. This behavior is in contrast with the frequency independent behavior of $T_i$, for a very long temperature range in the isotropic phase. Measurements between 7 MHz to 30 kHz in PAA, show this critical behavior, indicating the short-range order fluctuations (called cybotactic clusters) in the isotropic phase close to the I-N phase transition. Order fluctuations loose their importance, once the long-range nematic order is formed in the medium.

In the nematic phase sufficiently away from the phase transition temperature, director fluctuations (DF) become very important. The experimental efforts by Doane...
et al., [15] and Blinc et al., [14] could not lend them to a single interpretation on frequency dependent 7, data of MBBA (10.4) The limited frequency NMRD studies (from 4 MHz to 100 MHz) on 10.4, by Doane et al., favored the DF domination whereas Blinc et al., had recommended the SD domination Both the groups had come up with different arguments for corresponding behaviors in order to eliminate the difficulties in fitting the NMRD data. Doane et al., had proposed a high frequency cut-off for DF modes, and Blinc, a step-width parameter for SD mechanism. Doane remodified his theory considering both DF modes and local diffusive reorientations of proton spins, which lead to a cross correlation term also But the proton NMRD work using the field-cycling technique on MBBA and other systems by Noack’s group [11] established the fact that, SD and R are the very important dynamical processes in conventional NMR frequencies in nematic liquid crystals, and DF modes are more effective at low frequencies Anisotropy can be best probed by the angular dependent spin relaxation studies, and the angular dependent NMRD studies by Noack et al., [11] established the effect of local fields beyond doubt, and permitted a detailed analysis of DF at low frequencies

6.1.5. Experimental Details

In this sub-section an attempt is made to give general experimental details like sample preparation, pulse sequences used in NMRD data collection, theoretical models, fitting procedures, data analysis etc, in order to avoid repetition of the same details when each liquid crystal system is discussed in the forthcoming sections.

The 4O.m samples were purchased from a commercial source (M/S Frinton Laboratories, USA) and used without further purification Samples were sealed under vacuum (10⁻⁵ Torr) after removing the dissolved oxygen, by the freeze-pump-thaw method. Phase transition temperatures were verified with the observed changes in the amplitude and shape of the FID In order to orient the nematic director \( n \) of the system, parallel to the Zeeman magnetic field, the samples were heated to the isotropic phase first, and slowly cooled to the temperature in the presence of the Zeeman magnetic field Proton NMRD data were collected in the nematic phases at fixed temperatures using the FCNMR spectrometer The temperature dependent data
collected earlier in this laboratory [1,2] was also used in the analysis in order to get a complete picture on the dynamical properties in different mesophases.

The inversion-recovery \( rf \) pulse sequence and the saturation-burst \( rf \) pulse sequences were used on the conventional pulsed NMR spectrometer. Inversion recovery sequence and single pulse methods were used on FCNMR spectrometer. The details of the pulse sequences and the data fitting procedures are presented in chapter 1. The estimated errors in \( T_I \) measurements at frequencies below 1 MHz are found to be less than 7\%, and at above 1 MHz there are around 5\%.

6.1.6. Data analysis

It has been established that, the proton \( T_I \) measurements are expected to show dominant contributions to \( J_{i}(\omega) \) from the three mechanisms (DF, R and SD), which are essentially distinguished by their characteristic frequency dependent behaviors. Effective contributions to the spectral densities from these dynamics could be seen at the Larmor frequency and at twice the Larmor frequency. The total spin lattice relaxation rate \( (R_{1Tot}) \) therefore, can be written as

\[
R_{1Tot} = R_{1DF} + R_{1SD} + R_{1R}
\]  

(6.1)

Detailed expressions for each contribution are given in chapter-5. The data were analyzed, fitting them to the above equation 6.1, using the non-linear least square analysis, based on the Levenberg - Marquardt algorithm [52].

6.1.6.1. Nematic Director fluctuations (DF)

The data analysis was done using two different procedures for the DF contribution. The first method is based on the one constant approximation (isotropic elastic constants model). The second method is based on the anisotropic elastic constants model, using a generalized expression [18] incorporating all the modifications made by Doane and Johnson [15], Brochard [53] Vold and Vold [16].
and Blinc et al., [14] on the Pincus model [17]. In the present NMRD data analysis, the generalized equation for DF modes [18] is used for both the analysis

### 6.1.6.1.1. Isotropic elastic constants model

In the first method, elastic constants are fixed as $K_{11} = K_{22} = K_{33} = 10^6$ dyne. For the *director fluctuations* with lower and upper cut-off frequencies, the model parameters are the amplitude $A_{\text{dir}}$, lower cut-off frequency $\nu_{\text{loc}}$, and upper cut-off frequency, $\nu_{\text{hch}}$. The well known square-root frequency dependence on the relaxation time between upper and lower cutoff frequencies is the basis for the identification of the DF contribution. Details of the theoretical formulation of this model are given in chapter-5, section 5.2.

### 6.1.6.1.2. Anisotropic elastic constants model

In the second procedure (called the *anisotropic elastic constants model* or *generalized model*) an expression, considering the influence of upper and lower cut-off wavelengths for the director modes, as well as the anisotropy in elastic constants were used in calculating the DF parameters. Based on this model the relaxation rate due to director fluctuations ($R_{\text{DF}}$) is given by [18]

$$R_{\text{DF}} = A_{\text{DF}} \sum_{\nu} \frac{\sqrt{\eta_\nu}}{K_{\nu} \sqrt{\eta_{\nu}}} \left[ f(P_{ab} \cdot A_{ab}) - f(P_{ab} \cdot A_{ab}) - f(B_{ab} \cdot A_{ab}) + f(B_{ab} \cdot A_{ab}) \right]$$  \hspace{1cm} (6.2)

where

$$A_{\text{DF}} \propto f(\Delta) \frac{2\eta_\nu^2 k_\nu f}{(2\pi)^2}$$

The cut-off frequencies are given by

$$\nu_{\text{loc}} = \frac{K_{\nu} q_{\text{loc}}^2}{2\pi \eta_\nu} \quad \text{and} \quad \nu_{\text{hch}} = \frac{K_{\nu} q_{\text{hch}}^2}{2\pi \eta_\nu}$$
The complete description of the functions and parameters involved in this model has also been described in chapter-5. The experimental elastic constants measured by Tolmachev et al., [30] for 40.4 are used in deducing the elastic constants for other 4O.m systems. These elastic constants are given as the input parameters in the model for the DF contribution. It is known that $S$ (order parameter) is proportional to the square of the density [31] and the anisotropy of the refractive index [33]. Elastic constants are proportional to $S^2$ [32].

A systematic study of the refractive index and density on 4O.m systems by Potukuchi [7] were used in estimating the relative values of $S$ in 4O.m systems. Using 4O.4 elastic data as the reference, the values of the elastic constants for other 4O.m systems were calculated, following the variations in the density and refractive index values at required temperatures. Figure 6.4, shows the density variations in the 4O.m systems.

Figure. 6.4. Densities near isotropic-nematic phase transition in 4O.m systems [7].
The general trend of decreasing density with increasing chain length, as well as the odd-even alteration, is observed in these phases. The system with symmetric end chains shows an increase of density in the isotropic as well as in nematic phases. The density decreases with the increasing alkyl chain length. Odd and even systems follow smooth curves [7] in the isotropic and nematic phases with temperature. There is no slope change in the interface between the nematic to smectic A transition when the alkyl chain is short. The systems 40.8, 40.6, 40.4, as well as 40.5 and 40.7, show no slope change at the interface.

The density data in the interface between the S_A-S_B also [7] shows a very different behavior from that of the I-N interface. Odd systems show high values of density in both S_A and S_B phases. Near the transition, all even systems except 40.8 show a linear behavior. 40.8 shows a lower value than the expected value. The system 40.9 also deviates from the linear behavior with respect to the other odd systems. In general, symmetric end chain systems show higher densities. Figure 6.5 shows anisotropy in the refractive index of the 40 m systems.

![Anisotropy in the refractive index as a function of reduced nematic temperature T in the 40 m systems.](image)

Figure 6.5 Anisotropy in the refractive index as a function of reduced nematic temperature $T_N$ in the 40 m systems [7].
The data were plotted as a function of reduced temperature, $T_N$ [7] such that one can easily compare the behavior of refractive index anisotropy in all the nematic phases, which have nematic phases in different temperature regions. It is interesting to note that the refractive index data shows a completely different behavior when compared to the density data, within the 40.m homologous series. Though the general trend of decreasing density and decreasing anisotropy with chain length is observed, the refractive index anisotropy shows very strong anomalies which could not be explained by the simple packing effects (chain length effects) or by odd-even effects.

The NMRD data were analyzed, considering the equations (5.62-5.67 for DF) given in chapter-5, under certain assumptions, to reduce the number of parameters to be determined from the data. The values of viscosity coefficients $\eta_1$ and $\eta_2$ were assumed to be 0.5 P. Though these values differ from compound to compound and are temperature dependent, the order of magnitude remains the same, if the molecular structure is essentially similar. Further, since these quantities appear as ratios $K/\eta$ in $R_{1DF}$, its variation should be much less from the assumed values [13]. In addition, since the long wavelength cut-off values of DF modes should not depend on the anisotropy at molecular level, it was also assumed that $\lambda_{zch} = \lambda_{\perp ch}$. Then four parameters connected with $R_{1DF}$, viz. $\lambda_{zlL}, \lambda_{zg}, \lambda_{zch}$ and $ADF$ are left to be evaluated from the data. The parameters $K_{11}, K_{22}$ and $K_{33}$ are given as input parameters. In the fitting program, the input variables connected with the cut-off wavelengths are given in terms of wave vectors ($q$'s). The equations connecting wave vectors, cut-off frequencies and cut-off wavelengths are also described in chapter-5. The subscript $l$ in the term $\lambda_{Lcl}$ refers to the direction perpendicular to the director. The subscript $p$ is also used often, with the same meaning of the subscript $l$. The subscript $z$ refers to the direction parallel to the nematic director.

### 6.1.6.2. Smectic layer undulation modes (LU)

In the case of smectic A phase, layering leads to a sudden increase of bend ($K_{ij}$) and twist ($K_{22}$) elastic constants. The strong mechanism, which influences the
spin relaxation at low Larmor frequencies are the layer undulation modes (LU). Theoretical formulation for this contribution and the parameters involved, are also described in chapter-5. **Important** parameters involved in fitting the NMRD data in the smectic A phase includes the upper and lower cut-off frequencies and the constant $A_{LU}$. In the present experimental NMRD data the contribution from LU is very small, due to the fact that the experiments are performed only from 50 kHz. The contribution from LU becomes very weak at this frequency. A presence of this contribution is essential however, to explain the NMRD data in the smectic A phase, particularly to explain the small region having a steep variation below about 200 kHz. The simplified equation used to fit the LU contribution is given here (equation 6.3) [48]

$$ R_{LU} = \frac{9}{8} \gamma^4 \hbar^2 J_1(\omega) = \frac{9}{8} \gamma^4 \hbar^2 \frac{A}{\omega} \left[ \arctan \left( \frac{\omega_l}{\omega} \right) - \arctan \left( \frac{\omega_u}{\omega} \right) \right] $$  \hspace{1cm} (6.3)

Where $\gamma$ is the gyromagnetic ratio for protons, $\hbar$ is the Planck’s constant divided by $2\pi$, $J_1(\omega)$ is the spectral density and $A$ is the adjustable parameter which depends on the temperature, nematic order parameter and material physical constants. $\omega_u$ and $\omega_l$ are the lower and upper cut-off frequencies of the collective modes, respectively, depending on the effective viscosity, splay elastic constant and smallest and largest wave vectors present in the system. This equation if further simplified by defining a new constant, $A_{LU}$, which is the new adjustable parameter given by

$$ A_{LU} = \frac{9}{8} \gamma^4 \hbar^2 A $$

The values of ALU’S obtained in present analysis are not accurate, since the NMRD data collected on smectic A phases have shown, a very short frequency region, having this linear behavior. In the present analysis, the functional behavior (linear behavior) is given priority rather than the other parameters such as cut-off frequency and the constant $A_{LU}$.
Various theoretical models used, to get information about the rotational dynamics, in the analysis of the NMR data are listed below [12].

- The simple Woessner approach [37] of rotating ellipsoids.
- The small-step rotational diffusion in the ordering potential proposed by Nordio and Brown [35].
- The anisotropic viscosity model [36] of Freed et al., in combination with fast spinning around the molecular long axis [16,34], the so called Void and Void's ‘third rate model’ and
- Extensions of Woessner’s formalism (and the small step rotational diffusional model) made by Dong et al., [12], with the inclusion of correlated uncoupled chain mobilities.

Graf et al., [4] have argued that the rotations about the short molecular axis are very significant in nematics since they are much slower than that of the rotations about the long axis. It has been argued that the rotations of segments and methylene groups occur parallel with the fast rotation, about the long axis and their contribution, moreover, is not important in NMR frequencies in the nematic phase. The correlation times obtained for rotations suggest that the rotations seen in the nematics are about the short molecular axis. For 10.4 the observed values of $\tau_R$ from NMRD studies are $2.4 \times 10^{-7}$ s at 18°C, and $5.7 \times 10^{-8}$ s at 45°C. These values are comparable with dielectric studies [13,41]. It is observed from dielectric experiments that the correlation time corresponding to the reorientation about a short molecular axis can have the value of the order of $10^{-6}$–$10^{-8}$ seconds [13]. Near the I-N transition all these motions (R, SD and DF) become equal at medium frequencies [4]. Based on the above observations made in the literature, rotations about the short axis are considered in the present analysis of nematic NMRD data.

In the case of rotations about the short molecular axis, the explicit model parameters used are, the amplitude $C$ and the rotational correlation time $\tau_R$, assuming a simple BPP type (Eq. 5.146) contribution. Rotations about the short molecular axis are important at high temperature nematic phase closer to the I-N transition. Since the
data is not collected above 50 MHz, and no attempt is made to collect angular dependent data, the more advanced models proposed by Nordio [35], Vold and Vold [34], Dong [12] and others were not implemented, for R contribution in the present NMRD analysis.

Apart from the contribution from rotations (R), with a single correlation time for the rotations about the short axis, it is expected that there are other rotational diffusive motions. It is assumed that in the present NMRD analysis between 50 kHz to 50 MHz these fast motions can contribute with a frequency independent behavior. Comparing with the strong SD contribution, which shows frequency dependence in the current frequency range, the faster rotations are difficult to detect. Keep in mind the importance of the parameters connected with the rotations about the short axis, and the complications involved in fitting so many parameters with the data available in the narrow frequency region. The contributions from faster rotations are not considered in model fitting. The three contributions, DF, SD and R about the short axis are sufficient to explain the present NMRD data in 40 m systems.

Smectic A Phase

In the present systems, NMRD data does not show discontinuity between nematic and smectic A phases in the conventional NMR frequencies. This shows that there are common mechanisms in nematic and smectic phases, which dominate spin relaxation in this frequency range. SD is one such mechanism, which dominates the conventional NMR frequency range. R about the short axis, seen in the nematic phases of these systems as well as the other rotational diffusive motions may also be present in the smectic A phase, owing to the fact that the smectic A phase is again a fluid like phase. The simple BPP type equation is used in fitting the R contribution in the smectic A phase too.

6.1.6.4. Self-Diffusion (SD)

Vilfan et al. [40] have developed a theory for SD in liquid crystals, which is a modified version of the Tonrey’s theory [39] developed for isotropic liquids, using
Chandrasekars' random flight model. Theoretical details of this model have been described in chapter-5. Significant observations made in the literature, useful in handling the NMRD data are discussed here.

It was generally found that the high frequency spectrum (from few tens of MHz to a few hundred MHz) of NMRD data was mainly determined by self-diffusion mechanism [11]. In the case of self-diffusion, the model parameters are B (the amplitude), and D (the average diffusion constant). In the present NMRD studies, the complete profile of the diffusion curve could not be obtained due to lack of data at high frequencies, above 50 MHz. Same equation (5.136) is used for SD mechanism in both nematic and smectic phases.

In order to avoid mistakes in calculating the SD constants, restrictions are imposed [4] on the jump time $\tau_{SD}$, by providing the average self-diffusion constant suited to the isotropic approximation of $R_{1SD}$, and by imposing the Einstein relation $D=\frac{6}{\tau_{SD}}$. The low frequency asymptote $T_{JSD}$ ($\omega \rightarrow 0$) and the dispersion frequency $1/(2\pi\tau_{SD})$ are correlated thus, i.e., in the fit they cannot be shifted independently.

6.1.7. Ordered smectic Phases

Dynamic mechanisms identified, which are responsible for relaxation in N, $S_A$ and $S_C$ phases are different from the mechanisms identified for relaxation in SB, $S_G$ and other solid smectic phases. In the N, $S_A$, and $S_C$ phases the important mechanisms, along with the nematic DF modes and smectic layer undulation modes, are SD and R about the short axis. In the case of ordered smectic phases and solid phases of the liquid crystalline materials, the contribution from DF and LU becomes negligible, in the frequency region of interest. Different types of rotations along with the SD mechanism are important in these phases. This argument is well supported by the $T_1$ and $T_{1D}$ measurements made by Heinze and Grande [41] on nO.m systems. The negligible discontinuities of temperature dependent F/ data in the N-$S_A$ and $S_A$-$S_C$ transition regions and an almost non-discontinuity in the $T_{1D}$ values at these transitions supports this view.
The observed jumps at the transition to $S_{II}$ or $S_{G}$ phases in both $T'_{II}$ and $T_{I}$ at frequencies between 5-50 MHz [41] clearly demonstrates the difference between the dynamic properties of the highly ordered smectic phases (B and G) and the fluid-like smectic phases (A and C) in the long chain systems for example, in 70.4, temperature dependent $T$ and $T'_{II}$ studies at 32 MHz were carried out by Heinze and Grande [41], in the temperature range from 60° C to −150° C. This work clearly demonstrates the typical motational processes responsible for spin relaxation in the highly ordered phases. The $T$, data can be described based on the following observations made by these studies [41]. The typical behavior of the temperature dependent $T'_{II}$ and $T_{I}$ data obtained from these studies are shown in figure 6.6.

Figure 6.6 Typical behavior of $T'_{II}$ and $T_{I}$ data as a function of temperature in the system. 70.4 Theoretical curves explaining the behavior of the data are also shown in the figure [41].
Different temperature regions of the $T_1$ data shown in figure 6.6 and their theoretical explanation are given below.

- In the high temperature (smectic G or Smectic B phase) region, called region-III, the decrease with decreasing temperature. This region is explained by the rotation of the molecule as a whole (with a single correlation time $3 \times 10^{-9}$ s at $-18^\circ$C, with an activation energy of about 8 kcal/mole) about the long axis. A minima in the $T_1$ is seen at about $-15^\circ$C.

- The relaxation in the next region from $-25$ to $-105^\circ$C (region-II) is due to the chain segmental motions. A minima is seen around $80^\circ$C, due to chain segmental motions.

- The lowest temperature range (region -I) showing a minima at around $-130^\circ$C in the $T_1$ data is due to the three-fold CH$_3$ reorientation (with a correlation time of $3 \times 10^{-9}$ s at $133^\circ$C with an activation energy of about 2kCal/mole). Region-I overlaps with region-II and similarly, region-II overlaps with region-III. At any temperature, different contributions to spin relaxation could be separated out by fitting the $T_1$ data to an equation considering these mechanisms.

Similarly, different temperature regions of the $T_{1D}$ data obtained from 70.4 are also shown in figure 6.6 and their theoretical explanation are given below [41].

- The high temperature region (region -III') of $S_G$ and $S_B$ phases (from $60^\circ$C to $-20^\circ$C) SD mechanism with a correlation time of about $10^{-5}$ s and an activation energy of about 12 kcal/mole is observed ($S_B$ showing higher correlation time).

- The lower temperature region (region-II') of $T_{1D}$ data is explained by the rotation of the whole molecule. The lowest temperature region (region-I) in the $T_{1D}$ data, is explained using intra molecular rotations.

These observations are useful in explaining the temperature dependent $T_1$ data in the ordered smectic phase. In the present experimental studies, no model fitting was attempted to explain the temperature dependent $T_1$ data of smectic B, or smectic G phases. But, the NMRD data is analyzed, considering the contributions from rotations and diffusion. From these observations, it is natural to expect SD domination at low frequencies and rotations about the long axis, at conventional NMR frequencies in these phases.
6.2. NMRD study of Butyloxybenzylidene ethylaniline (4O.2)

The first system studied in the 4O.m series is butyloxybenzylidene ethylaniline (4O.2). 4O.2 has the phase sequence given by [6],

\[
\begin{align*}
39 \degree C & \quad 51.5 \degree C & \quad 66 \degree C \\
X & \quad S_G & \quad N
\end{align*}
\]

This system has a stable nematic phase over 14.5 \degree C and an ordered smectic G phase over 9 \degree C. between an isotropic liquid phase and a solid phase.

6.2.1. Experimental Details

Proton NMRD measurements were carried out as a function of frequency in the nematic phase of 4O.2, at temperature 61 \degree C. The data from 55 kHz to 3 MHz was obtained, using the field-cycling NMR spectrometer, and the high frequency data from 3 to 50 MHz was obtained using a conventional NMR spectrometer [2]. The estimated error in measurements at frequencies below 1 MHz is found to be less than 7% and at above 1 MHz it is around 5%. NMRD data from 55 kHz to 50 MHz at temperature 61 \degree C in the nematic phase of 4O.2, is illustrated in figure 6.7. The observed NMRD data in the nematic phase of 4O.2 has the following features.

1. The relaxation times are range from 52 milliseconds at 55 kHz. to 444 milliseconds at 50 MHz. and decreases with decreasing frequency in the entire frequency range, studied.

2. \(7/\) data in the logarithmic scale (figure 6.7) shows a steep variation as a function of Larmor frequency. At low proton Larmor frequencies, the data shows a longer region having a square-root behavior, which extends up to intermediate frequencies, indicating the presence of the DF mechanism at this frequency range. The NMRD data slightly
deviates from this behavior from 2 MHz and a slightly different slope was observed at higher frequencies.

Figure 6.7. Frequency dependence of the spin-lattice relaxation time ($T_1$) in the nematic phase of 40.2 at temperature 61 °C.

3. Thus, the NMRD data in the nematic phase of 40.2 at 61 °C, shows two different regions with different slopes, and hence, a look at the data suggests that there are at least two possible mechanisms with different frequency dependence. The temperature dependent data at spot frequencies at 5, 9, 15, 19.5, 29.8, and 50 MHz are shown in figure 6.8.

In the conventional NMR region, the temperature dependent $T_1$ data shows an interesting behavior with two different regions in the nematic phase, from 5 MHz to 50 MHz. The first region close to the I-N phase transition shows almost a constant $T_1$ value with a lowering of the temperature. This trend continues for about 10 °C at lower frequencies. This region close to the I-N phase transition becomes shorter in the case of higher frequency data from 30 MHz onwards. The second region, with strong temperature dependence is observed closer to the N-SG transition. The nematic phase range having strong temperature dependence in $T_1$ data is longer at high frequencies,
rather than low frequencies. This trend suggests that the SD mechanism becomes more dominant only at higher frequencies around 30 MHz. SD necessarily dominates the nematic phase near the N-S$_g$ transition in all frequencies, from and above 30 MHz.

Figure 6.8. The behavior of the spin-lattice relaxation time ($T_1$) as a function of temperature at different frequencies in 40. The arrows denote the transition temperatures.

A sudden increase of $T_1$ is observed near the nematic to smectic G phase transition. Data in the ordered S$_{G_3}$ phase shows strong temperature dependence as well as frequency dependence in the conventional NMR frequency range. $T_1$ decreases with an increase in temperature, and decreases, with a decreasing frequency. It is interesting to note a minimum in the temperature dependent data at each frequency in an ordered smectic G or solid phase. The minimum observed at a lower temperature at the lowest frequency (5 MHz) shifts towards a higher temperature in the higher frequencies (50 MHz).
6.2.2. Data analysis

6.2.2.1. Nematic Phase

6.2.2.1.1. Isotropic elastic constants model

The frequency dependent relaxation rates \((R_I - I T_I)\) at 61 °C, in the nematic phase of 40.2, were fitted to an equation assuming contributions from all the three dynamic processes namely SD, R and DF. The DF contribution to the NMRD data was fitted in two different ways. The value of \(A_{DF}\) and the lower cutoff frequency were varied to get a good fit. The DF contribution is quantified by the constant \(A_{DF} = 6.68 \times 10^{-6} \text{ s}^2\) in the case of the one constant approximation method. The estimation of upper cut-off frequencies becomes complicated, since the DF contribution becomes negligible at the expected cut-off frequency ranges. In the present case, the upper cut-off frequency should be above than 100 MHz, assuming the molecular length to be the parameter deciding this cut-off. The lower cut-off frequency is about 8.1 kHz, and the corresponding upper cut-off wavelength for the director modes is about 3927 °A.

The dynamic parameters obtained from this fit are summarized in table 6.1. The qualitative picture of the fitting, in the nematic phase of 40.2, reveals that the DF dominates the spin relaxation up to 5 MHz. Relative contributions of DF, R and SD are shown in figure 6.9. The \(T_I\) data at 5 MHz shows almost no temperature dependence, which is attributed to the strong contribution from the DF mechanism. Rotations (R) about the short axis shows a frequency independent behavior ranging from 50 kHz to 5 MHz. A frequency dependent behavior of R, up to 30 MHz also contributes to the spin relaxation, along with the DF and SD. SD is more important than R throughout the dispersion. The DF mechanism becomes weaker, from 30 MHz onwards. The increasing slope of temperature dependent data, with an increasing frequency above 30 MHz also supports this view.
Figure 6.9. Proton relaxation rate \( R_I = 1/T_I \) as a function of frequency in the nematic phase of 4O.2 at 61 °C and the model fit to three individual contributions to the relaxation rate director fluctuations (DF), self-diffusion (SD), and molecular reorientations about the short axis (R). The isotropic elastic constants model is assumed for DF contribution.

The NMRD data fitting gives the relative contribution of the various dynamical processes at different frequencies. A more quantitative picture of the relative contributions can be obtained at different frequencies by calculating the percentage contribution due to various mechanisms. For example at 50 kHz, the contribution from the DF mechanism to the total relaxation is about 84%. The contribution from R and SD are about 4% and 12% respectively. The contributions at 1 MHz are 56% due to DF, 33% due to SD and 11% due to R. Contribution from SD becomes more important than DF, above 5 MHz. The contributions at 5 MHz are 41% due to DF, 52% due to SD and 7% due to R. At 10 MHz the contribution from R becomes 3% only. DF and SD contribute 35% and 62% respectively, to the spectral density. At
20 MHz, the DF contribution becomes 28.5% and the remaining 70.5% relaxation is almost due to the SD mechanism, and 1% is from R. At the maximum measured frequency (50 MHz) the contributions from SD and DF are 78% and 22%, respectively.

**Reorientations about the short molecular axis**

In the case of *rotations about the short molecular axis*, the explicit model parameters used, are the amplitude C and the rotational correlation time $\tau_R$, assuming a simple BPP type contribution, neglecting the effects, due to molecular anisotropy. The values obtained for the R mechanism is given in the table 6.1. The correlation time obtained for rotations about the short molecular axis in the nematic phase of 40.2 is $5.53 \times 10^{-9}$ seconds. The contribution to the total relaxation rate from $R_\phi$ is given by the value $C = 10.9 \times 10^7 \text{ s}^{-1}$. Rotations about the molecular short axis seem to be temperature independent or weakly temperature dependent, in the nematic phase.

**Self-Diffusion**

In the case of *self-diffusion*, the model parameters obtained are given in table 6.1. The parameter $B$, is equal to $4.2 \times 10^3 \text{ s}^{-2}$, the average diffusion constant $D$ is obtained as $2.63 \times 10^6 \text{ m}^2 \text{ s}^{-1}$. The frequency independent contribution from SD is restricted to lower frequencies upto 10 MHz, in the nematic phase of 40.2. The stronger temperature dependence observed in the high frequency data can be accounted by the presence of SD process at high frequencies.

**6.2.2.1.2. Anisotropic elastic constants model**

In the second procedure, an expression considering the influence of upper and lower cut-off wavelengths for the director modes as well as, the anisotropy in elastic properties was used in calculating the DF parameters. The complete description of the functions and parameters involved in this generalized model have been described in chapter 5. The experimental elastic data obtained for 40.4 [30] is used to get elastic
data for 40.2, by extrapolation. The elastic constants calculated for 40.2
\(K_{II} = 1.2 \times 10^6\), \(\Delta V = 0.812 \times 10^6\) and \(K_{zz} = 1.76 \times 10^6\) dyne) at 61 °C are used in the model fitting. The details of the calculation of the elastic constants are given in the section 6.1. The fitting is shown in figure 6.10.

Figure 6.10. Proton relaxation dispersion (\(R_i = 1/T_i\)) data as a function of frequency in the nematic phase of 40.2 at 61 °C and the model fit to three individual contributions to the relaxation rate: director fluctuations (DF), self-diffusion (SD), and molecular reorientations about the short axis (R). The anisotropic elastic constants model is considered for DF contribution.

The constant \(A_{101}\) obtained for 40.2 is \(4.3831 \times 10^{-6}\) s\(^2\), a value smaller than that obtained from the isotropic elastic constants model. The lower cut-off frequency in this case is less than 1 kHz. The upper cut-off frequencies in the directions parallel and perpendicular to the director are \(1.2 \times 10^8\) Hz and \(9.95 \times 10^8\) Hz, respectively. The parameters obtained from both these methods are given in table 6.1.
The contributions obtained for SD and R are different from the picture obtained from the isotropic elastic constants model. The values of B and D are decreased. Correlation time for rotations is increased by an order of magnitude. In this case, the DF contribution dominates for upto 3 MHz, with the square root behavior.

Table 6.1

<table>
<thead>
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<th>Model Parameters</th>
<th>Isotropic elastic constants model</th>
<th>Anisotropic elastic constants model</th>
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<tr>
<td>Nematic director fluctuations (DF)</td>
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<tr>
<td>$K_{11}$ (in $10^6$ dynes)</td>
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</tr>
<tr>
<td>$K_{22}$ (in $10^6$ dynes)</td>
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<tr>
<td>$K_{33}$ (in $10^6$ dynes)</td>
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<td>$\lambda_{zecl}$ (in A)</td>
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<td>$B$ (in $10^9$ s$^2$)</td>
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<tr>
<td>$D$ (in $10^{-10}$ m$^2$ s$^{-1}$)</td>
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<td>1.98</td>
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<td>Rotations about the short axis (R)</td>
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<tr>
<td>$C'$ (in $10^8$ s$^{-2}$)</td>
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<tr>
<td>$\tau_R$ (in $10^{-9}$ s)</td>
<td>5.53</td>
<td>24.4</td>
</tr>
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Self-diffusion (SD) mechanism, which is frequency independent up to 3 MHz, becomes responsible for the frequency dependence seen in the experimental NMRD data, above 3 MHz SD is strong at higher frequencies than at frequencies below 10 MHz Temperature dependent data above 10 MHz, shows a stronger variation, due to the increased domination of the SD. Rotations about the short axis show frequency independent behavior up to 1 MHz and then, becomes frequency dependent up to 10 MHz

6.2.2.2. Ordered smectic phase ($S_{11}$)

The observed increase of $T_1$ at the transition from nematic to the smectic G phase of 40.2, in the frequency range between 5-50 MHz, clearly demonstrates the basic difference between dynamic properties of the highly ordered smectic G phase and the fluid-like nematic phase. Slowing down of the diffusion process and the absence of the DF mechanism are responsible for the sudden increase of $T_1$ in the smectic G phase in the conventional NMR frequencies. In the smectic G phase of the 40.2, $T_1$ data shows strong temperature dependence.

Using the detailed experimental observations made by Grande and Henize [24] in the nO.m systems, it is possible to qualitatively explain the present temperature dependent $T_1$ data in the ordered smectic phases and solid phases. The typical behavior shown by nO.m systems earlier has been described in the previous section. From the present behavior of the data in the $S_{11}$ phase at the measured temperature ranges, one can conclude that the major contribution comes from rotations of the molecule around the long axis and from segmental motions.

Since there are two terminal chains and many CH$_3$ groups present in the 40.2 system, several rotational diffusion modes could be present, leading to as many values of the correlation times possible. The frequency dependent $T_1$ data measured in the $S_{11}$ phase supports this view. This contribution is responsible for the frequency dependence in the $S_{11}$ phase at conventional NMR frequencies from 10 MHz to 45 MHz.
6.3. NMRD study of Butyloxybenzylidene propylaniline (4O.3)

The next system, studied in the 4O. m homologous series is butyloxybenzylidene propylaniline (40.3). It has the phase sequence given by [42]

\[ 54 \, ^\circ C \quad 82.5 \, ^\circ C \]

\[ X \longrightarrow N \longrightarrow I \]

A stable, very wide nematic phase (28.5 °C) was observed between isotropic (I) and solid (X) phases in 40.3.

6.3.1. Experimental Details

Proton spin-lattice relaxation time \((T_i)\) measurements were carried out as a function of Larmor frequency in the nematic phase of 40.3 at temperature 69 °C. The data from 50 kHz to 3 MHz were obtained using the field-cycling NMR spectrometer, and the high frequency data from 3 to 50 MHz were obtained using a conventional NMR spectrometer [2]. The errors in \(T_i\) measurements at frequencies below 1 MHz are found to be less than 7% and at above 1 MHz they are around 5%. Experimental NMRD data for the nematic phase is shown in figure 6.11. The temperature dependent data at spot frequencies 9, 15, 19.5, 29.8, 39.6, and 50 MHz is shown in figure 6.12. The observed NMRD data in the nematic phase of 40.3 has the following features.

1. The relaxation times range from 45 milliseconds at 65 kHz, to 550 milliseconds at 50 MHz. \(T_i\) increases with increasing frequency throughout the nematic phase.

2. \(T_i\) in the logarithmic scale varies slowly as a function of Larmor frequency, with a maximum slope in the low frequencies below 100 kHz. The slope decreases in the intermediate frequencies from 100 kHz to 800 kHz, and there is a steeper region after this (800 kHz to 3 MHz). Finally a region with a slow variation is seen from 6 to 40 MHz.
Figure 6.11. Frequency dependence of the spin-lattice relaxation time ($T_1$) in the nematic phase of 40.3 at temperature 69 °C.

Figure 6.12. The behavior of the spin-lattice relaxation time $T_1$ as a function of temperature at different frequencies in 40.3. The arrows denote the transition temperatures.
Thus, the NMRD data in the nematic phase of 40 at 69 °C, shows at least three different regions with different slopes. Hence, a first look at the data suggests that there are three possible mechanisms with different frequency dependencies.

In the conventional NMR region from 5 MHz to 50 MHz, the \( T_1 \) data shows a strong temperature dependence (the \( T_1 \) in the nematic phase decreases by more than 100 ms between the maximum or minimum temperature, at all the frequencies). This dependence becomes stronger at higher frequencies, making the 50 MHz temperature dependent data to show a higher slope than the 5 MHz data. This trend indicates that the major mechanism is probably self-diffusion, which should be stronger, at higher frequencies.

\( T_1 \) shows a sudden jump towards a higher value at the nematic to crystal phase transition and decreases quickly with temperature. The data in the crystal phase also shows strong frequency dependence. The \( T_1 \) value increases with frequency and decreases with temperature, within the frequency. A minimum is observed in the temperature dependent data, which moves towards the lower temperature region, when the frequency is lowered. The minimum seen at 28 °C at 5 MHz moves to 34 °C at 50 MHz. With regard to the general trends in the \( T_1 \) profiles, this behavior in the solid phase differs from the other solid systems under study, which would be discussed in the subsequent sections.

### 6.3.2. Data analysis

#### 6.3.2.1. Nematic Phase

6.3.2.1.1. Isotropic elastic constants model

The frequency dependent relaxation rates \((R - 1/T_i)\) at 69 °C in the nematic phase of 40.3 were fitted to an equation assuming a contribution from all the three dynamic processes, viz., SD, R and DF. The DF contribution to the relaxation was fitted in two different ways. The first method is based on the one constant
approximation, assuming $K_{11} = K_{22} = K_{33} = 1 \times 10^6$ dyne. The value of the constant $A_{DF}$ and the cut-off frequencies for the DF modes were varied to get a good fit. The DF contribution is quantified by the constant $A_{DF} = 3.2122 \times 10^{-6} \text{ s}^{-2}$.

Figure 6.13. Proton relaxation rate ($R_i = 1/T_i$) as a function of frequency in the nematic phase of 40.3 at 69 °C and the model fit to three individual contributions to the relaxation rate: director fluctuations (DF), self-diffusion (SD), and molecular reorientations about the short axis (R). The isotropic elastic constants model is assumed for DF contribution.

The lower cut-off frequency is about 412 Hz, and the corresponding upper cut-off wavelength for the director modes is about 17450 A. A constant value corresponding to lower cutoff wavelength of about 10 A was given for upper cut-off frequency in the model fitting in order to get a good fit. The NMRD fitting is shown in figure 6.13. The dynamic parameters obtained from this fit are summarized in table 6.2. A qualitative picture of the fit in the nematic phase of this system reveals that the DF modes completely dominate the spin relaxation at very low frequencies (in the kilo Hertz regime) and SD becomes significant from about 6 MHz. From 6.5 MHz
onwards, diffusion dominates the DF mechanism and it solely responsible for relaxation above 30 MHz

<table>
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<td>(K_{11}) (in (10^{-6}) dynes)</td>
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<td>(q_{ich}) (in (10^7) l/Am)</td>
<td>6.4</td>
<td>6.4</td>
</tr>
<tr>
<td>(f_{ich}) (in MHz)</td>
<td>1300</td>
<td>1300</td>
</tr>
<tr>
<td>(\lambda_{ich}) (in A)</td>
<td>9.81</td>
<td>9.81</td>
</tr>
</tbody>
</table>

Translational self-diffusion (SD)

| \(B\) (in \(10^V\)) | 6.386 | 6.409 |
| \(D\) (in \(10^{-10}\) m\(^2\) s\(^{-1}\)) | 5.07 | 5.42 |

Rotations about the short axis (R)

| \(\tau\) (in \(10^8\) s\(^{-2}\)) | 0.30 | 0.286 |
| \(\tau_R\) (in \(10^9\) s) | 119 | 112.56 |

Rotations about the short axis seem to be more important than diffusion below 1 MHz and become negligible above 2 MHz. At the conventional NMR frequencies, SD mechanism is very important. This interpretation is also supported by the strong
temperature dependence of the $T_1$ data at conventional NMR frequencies in the nematic phase.

A more quantitative picture of the relative contributions can be obtained by calculating the percentage contribution at different frequencies, due to various mechanisms. For example at 100 kHz, the contribution from DF mechanism in the total relaxation is about 82%. The contribution from SD and R are about 6% and 12% respectively. At 500 kHz, the contributions from DF, R and SD are about, 59.6%, 26%, and 14.4% respectively. The contributions at 1 MHz are 57.2% from DF, 24.3% from SD and 18.5% from R. The SD mechanism takes over the R mechanism from about 1 MHz onwards. This trend continues, and finally R becomes negligible right from 2 MHz. The contributions at 2 MHz are 52% due to DF, 36% due to SD and 12% due to R. At 6 MHz, DF modes and SD mediate spin relaxation equally and there is no contribution from rotations about the short molecular axis. At 20 MHz, it is estimated that the contribution from DF becomes one third and SD contributes the remaining two-thirds to the spectral density. Accuracy of various parameters differ widely, since the optimization procedure has to handle many parameters which have analytical dependence, and also because some of these constants are strongly correlated. In the present analysis the errors estimated for the model parameters are about 10%.

**Reorientation’s about the short molecular axis**

In the case of rotations about the short molecular axis, the explicit model parameters used, are the amplitude C and the rotational correlation time $\tau_R$. Since there is no region in the NMRD data where one can see the frequency behavior recommended for rotations, the deviations from the square root dependence is only an indication of the presence of rotations. It is not very difficult in the case of 40.3, with two steps seen at high frequencies. The SD should, in principle, take care of high frequency dispersion. The values obtained are given in table 6.2. The correlation time obtained for rotations about the short molecular axis in the nematic phase of 40.3 is $1.19 \times 10^{-7}$ seconds. It is observed from the dielectric experiments [33,34,41] that in the
presence of the nematic orientational order the correlation time corresponding to the reorientation about a short molecular axis can have correlation times of the order of $10^{-8}$ to $10^{-6}$ seconds

**Self-Diffusion**

In the case of **self-diffusion**, the model parameters are $B$ (the amplitude), and $D$ (the average diffusion constant). The theory and equations have been given in chapter 5. The frequency independent contribution from SD changes to frequency dependent, from 10 MHz. The complete profile of the diffusion curve could not be obtained due to the lack of data at high frequencies above 50 MHz. The strong temperature dependence at the highest frequency of 50 MHz, the $\gamma$ data observed, is due to the strong domination of SD process. The diffusion constant $D = 5.07 \times 10^{10} \text{ m}^2 \text{ s}^{-1}$ obtained here is in good agreement with the diffusion constants obtained for typical nematic liquid crystals [43].

6.3.2.1.2. Anisotropic elastic constants

The complete description of the functions and parameters, involved in this generalized model [18] have been described in chapter 5. The experimental elastic data given by Tolmachev et al., [30] for 40.4 is extrapolated, keeping in mind the general trends followed by other homologous series of nematic liquid crystals, in order to obtain elastic constants for the 40.3 system. It is well known that $K \propto S^2$ and hence the value of $ADF$ is attributed to the changes in the value of $S$ also. In this model, the $ADF$ value obtained is $3.53 \times 10^{-6} \text{ s}^2$, which is not very different from the value obtained from the isotropic elastic constant model.

The lower cut-off frequency in this case is 557 Hz, close to the value obtained from the one constant elastic constants model. The upper cut-off frequencies in the directions parallel and perpendicular to the director are same as that of the other model. The parameters obtained from both these methods are given in table 6.2. The correlation time obtained for rotations about the short molecular axis in the nematic
phase of 40.3, is $11.26 \times 10^8$ seconds. The contribution to the total relaxation rate from R is quantified by the value $C = 2.86 \times 10^7$ s$^{-1}$.

Figure 6.14. Proton relaxation rate ($R/T_1$) as a function of frequency in the nematic phase of 40.3 at 69 °C and the model fit to three individual contributions to the relaxation rate: director fluctuations (DF), self-diffusion (SD), and molecular reorientations about the short axis (R). The anisotropic elastic constants model is considered for DF contribution.

In the case of self-diffusion, the model parameter $B$ is equal to $6.409 \times 10^{10}$ s$^{-2}$, and $A$ the average diffusion constant is equal to $5.42 \times 10^{10}$ m$^2$ s$^{-1}$. Diffusion parameters ($B$ and $D$) obtained with the anisotropic elastic constants model for DF modes are almost the same as that of the parameters obtained in the case of the isotropic elastic constants model.

In comparison with the first model, the qualitative picture show differences, too. DF contribution in the second model is stronger than that of the first model. Diffusion does not change much, though the quantitative picture does show some
differences. The increase in DF is at the cost of reduction in the contribution from R only. Functional behavior of R does not change much, but the percentage contribution decreases from the value obtained from the first model. This increase in the DF contribution affects the percentage contribution of R and the value of B slightly. For example, the percentage contribution from SD at 50 MHz now, is about 8% lesser than the previous value. By performing the analysis using both models, a clear understanding of the role of elastic constants in the evaluation of the dynamic parameters can be had. It is very interesting to note that the value of $A_{DF}$ is strongly dependent on the anisotropy of the elastic constants.

### 6.3.12. Solid phase

In the solid phase, diffusion becomes negligible and DF modes are not possible. The increase in the relaxation times with decreasing temperature in the system 40.3 indicates that the hindrance to faster rotations (at higher frequencies) increase at lower temperatures. In the case of 40.3, the minima are close to the nematic to solid transition temperature for all the measured temperatures.

The relaxation in the highly ordered smectic phases and the solid phases can be best described, using three dynamical processes generally seen [24] in the chain molecules, 1. Rotation of the molecule as a whole around its long molecular axis, 2. Chain segmental motions and 3. CH$_3$ three fold rotations. Experimental relaxation rate in the solid system 40.3 can be explained, based on these contributions. The shifting of minima towards high temperatures with increasing Larmor frequency (strong minima at that frequency) could be interpreted as that, the reorientations about the long axis and the segmental motions could be better observed at high frequencies, when temperatures are high. In other words, the rotations about the long axis are faster at high temperatures, and hence, data at high frequencies have to be collected in order for their effect to be seen clearly. By decreasing the temperature, the reorientations about the long axis, can be slowed down, and the minima could be observed at the current (lower) frequencies.
6.4. NMRD study of Butyloxybenzylidene Butylaniline (40.4)

The next system in the 40.m series is \textit{butyloxybenzylidenebutylaniline} (40 4). This system has the phase sequence given by [6]

\[ 7^\circ C \quad 41^\circ C \quad 45^\circ C \quad 45.5^\circ C \quad 75^\circ C \]

\[ X \rightarrow S_G \rightarrow S_B \rightarrow S_A \rightarrow \text{N} \]

Stable \textit{nematic} (a range of 31 °C) and \textit{smectic G} (a range of 34 °C) phases along with a shorter smectic B (4.5 °C) and a very short smectic A phase (0.5 °C) are seen between the isotropic liquid and solid (X) phases. The mesophase range is very wide compared to the other shorter chain systems in the 40.m series.

6.4.1. Experimental Details

Proton spin-lattice relaxation time ($T_1$) measurements were carried out as a function of frequency in the nematic phase of 40.4 at a temperature of 67 °C. The data from 50 kHz to 3 MHz was obtained using field cycling NMR spectrometer and high frequency data from 3 to 50 MHz was obtained using conventional NMR spectrometer [2]. The estimated errors in $T_1$ measurements at frequencies below 1 MHz are found to be less than 7% and at above 1 MHz they are around 5%. It is important to mention here, that the temperature dependent data has strong pretransitional effects in the case of 40.4. Experimental NMRD data for the nematic phase, is shown in figure 6.15. The temperature dependent data at spot frequencies at 5, 9, 15, 20, 30, and 39.6 MHz are shown in figure 6.16. The observed NMRD data in the nematic phase of 40.4 has the following features

1. The relaxation times range from 51 milliseconds at 55 kHz to 413 milliseconds at 39.6 MHz. 7) decreases with decreasing frequency, as observed in the entire frequency range studied.
Figure 6.15 Frequency dependence of the spin-lattice relaxation time ($T_1$) in the nematic phase of 40.4 at temperature 67 °C. Data points are represented by circles. Error bars are also given along with the data points.

Figure 6.16. The behavior of the spin-lattice relaxation time ($T_1$) as a function of temperature at different frequencies in 40.4. The arrows denote the transition temperatures.
in the logarithmic scale shows variation as a function of Larmor frequency with lesser slope in the low frequencies (below 800 kHz). The slope increases in the intermediate frequencies (from 1 to 10 MHz) and finally reaches a region with lower slope in the higher frequencies (10 to 40 MHz).

Thus NMRD data in the nematic phase of 40.4 at 67 °C shows at least three different regions with very different slopes. The typical square-root behavior at low frequencies is very weak in 40.4.

In the conventional NMR region from 5 MHz to 39.6 MHz, the data shows an interesting behavior with three different regions. The first region close to the I-N phase transition shows an increasing value with the decreasing temperature. This trend continues for about 5 °C and the second region is seen with weak temperature dependence. This region continues for about 15 °C and the third region, showing very strong temperature dependence extending up to nematic to smectic A phase transition, is observed. The temperature independent region decreases with increasing frequency.

7) data shows a sudden increase towards a higher value at the smectic A to Smectic B phase transition. This value decreases with temperature after reaching a maximum value near the S to SQ phase transition. The data in the highly ordered S and S phases also shows strong frequency dependence. The 7) value increases with frequency and decreases with temperature within the frequency in the S phase. A region showing minima is observed in the temperature dependent data, which moves towards the lower temperature region, when frequency is reduced, in the S phase.
6.4.2. Data analysis

6.4.2.1. Nematic Phase

6.4.2.1.1. Isotropic elastic constants model

It is important to introduce the contribution from the rotation about the short molecular axis ($R$), in the analysis, in order to explain the low and intermediate frequency data up to 2 MHz. Similarly, the low frequency cut-off is necessary to fit the low frequency data in the kHz range satisfactorily. The frequency dependent relaxation rate ($R_{\text{IR}}$) at 67 °C, in the nematic phase of 40.4, is also fitted to two different models, the equation assuming contributions from all the three dynamic processes, viz., SD, R and DF.

![Proton relaxation rate as a function of frequency in the nematic phase of 40.4 at 67 °C and model fit (equation 6.1) to three individual contributions to the relaxation rate: director fluctuations (DF), self-diffusion (SD), and molecular reorientations about the short axis (R). Isotropic elastic constants are assumed in evaluating the DF contribution.](image)

Figure 6.17. Proton relaxation rate ($R_{\text{IR}}$) as a function of frequency in the nematic phase of 40.4 at 67 °C and model fit (equation 6.1) to three individual contributions to the relaxation rate: director fluctuations (DF), self-diffusion (SD), and molecular reorientations about the short axis (R). Isotropic elastic constants are assumed in evaluating the DF contribution.
Table 6.3

<table>
<thead>
<tr>
<th>Model Parameters</th>
<th>Isotropic elastic constants model</th>
<th>Anisotropic elastic constants model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nematic director fluctuations (DF)</td>
<td></td>
</tr>
<tr>
<td>$K_{11}$ (in $10^6$ dynes)</td>
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<td>0.9</td>
</tr>
<tr>
<td>$K_{22}$ (in $10^6$ dynes)</td>
<td>1</td>
<td>0.6</td>
</tr>
<tr>
<td>$K_{33}$ (in $10^6$ dynes)</td>
<td>1</td>
<td>1.3</td>
</tr>
<tr>
<td>$A_{1W}$ (in $10^6$ s$^{-2}$)</td>
<td>2.57</td>
<td>2.2988</td>
</tr>
<tr>
<td>$Q_{zel}$ (in $10^7$ 1/Am)</td>
<td>1.46</td>
<td>1.46</td>
</tr>
<tr>
<td>$F_{zel}$ (in kHz)</td>
<td>20</td>
<td>8.8</td>
</tr>
<tr>
<td>$\lambda_{zeh}$ (in A)</td>
<td>2480</td>
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</tr>
<tr>
<td>$Q_{zeh}$ (in $10^7$ 1/Am)</td>
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</tr>
<tr>
<td>$F_{zeh}$ (in MHz)</td>
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<td>900</td>
</tr>
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<td>$\lambda_{zcl}$ (in A)</td>
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</tr>
<tr>
<td>$Q_{jeh}$ (in $10^7$ 1/Am)</td>
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<td>5.64</td>
</tr>
<tr>
<td>$F_{jeh}$ (in MHz)</td>
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<td>1012</td>
</tr>
<tr>
<td>$\lambda_{jeh}$ (in A)</td>
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<td>11.14</td>
</tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Translational self-diffusion (SD)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B$ (in $10^9$ s$^{-2}$)</td>
<td>513</td>
<td>506</td>
</tr>
<tr>
<td>$D$ (in $10^{-10}$ m$^2$ s$^{-1}$)</td>
<td>363</td>
<td>318</td>
</tr>
<tr>
<td>Rotations about the short axis (R)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C$ (in $10^8$ s$^{-2}$)</td>
<td>1.245</td>
<td>1.238</td>
</tr>
<tr>
<td>$\tau_R$ (in $10^{-9}$ s)</td>
<td>5.816</td>
<td>5.878</td>
</tr>
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</table>

The value of $A_{1W}$ and the cut-off frequencies were varied to get a good fit. The DF contribution is quantified by the constant $ADF = 2.808 \times 10^6$ s$^{-2}$ in the case of one constant approximation method. This value for ADF is very less, since the domination of the DF contribution is confined to very low frequencies, and the higher frequency
dispersion is due to R and SD. The lower cut-off frequency is about 24 kHz, and the corresponding upper cut-off wavelength for the director modes is about 24800 Å. The typical errors estimated in evaluating the dynamic parameters are about 10%.

Relative contributions

Relative contributions from various mechanisms to the measured $R_1$ data are shown in figure 6.17. The dynamic parameters obtained from this fit are summarized in table 6.3.

A qualitative picture of the fit, in the nematic phase of 40.4 reveals that the DF modes dominate, spin relaxation at the very low frequencies up to 200 kHz. R about short axis dominates the relaxation with a frequency independent behavior from 200 kHz to 500 kHz and with a frequency dependent behavior up to 3 MHz. SD becomes important, from about 2.8 MHz, where all the three mechanisms become equally important. At high frequencies, diffusion is the major mechanism responsible for relaxation. This interpretation is supported by the strong temperature dependence of the $T_1$ data at conventional NMR frequencies throughout the nematic phase. The relatively weaker temperature dependence at intermediate frequencies, about 5 MHz is probably due to the presence of DF and R, along with the SD mechanism.

From the NMRD data fitting, the percentage contribution from various dynamical processes at different frequencies, can be calculated. For example at 55 kHz, the contribution from the DF mechanism to the total relaxation, is about 52.5%. The contribution from R and SD are about 36.5% and 11% respectively. At 100 kHz, the contributions from DF, R and SD are about, 48%, 40%, and 12% respectively. The contributions at 175 kHz are 43.2% from DF, 43.2% from R and 13.6% from SD. The R mechanism takes over the DF mechanism, from 175 kHz onwards. This trend continues, and finally R becomes equal to SD and DF at 2.8 MHz. The contributions at 1 MHz are 31% due to DF, 49% due to R and 20% due to SD. At 9 MHz, the contribution from R becomes 6% and SD contributes about 62% and DF contributes by about 32% to the spectral density. At the highest
measured frequency (39.6 MHz), DF contribution becomes very less (16.5%) and the remaining relaxation is almost due to the SD (about 83.5%) mechanism. This view is well supported by the strong temperature dependence of the 7 data at 39.6 MHz.

Reorientation’s about the short molecular axis

In the case of rotations about the short molecular axis, the explicit model parameters used are the amplitude C and the rotational correlation time $\tau_R$, assuming a simple BPP type contribution. The correlation time obtained for rotations about the short molecular axis in the nematic phase of 40.4 is $5.8157 \times 10^{-8}$ seconds. It has also been observed from the dielectric experiments that the correlation time corresponding to the reorientation about a short molecular axis can have the value of the order of $10^{-8}$–$10^{-7}$ seconds [41].

Presence of strong contribution from rotations about the short axis at kHz region is the mechanism, probably leading to the temperature dependent dipolar relaxation times ($T_{1//}$) [2]. Generally $T_{1//}$ shows temperature independent behavior when the DF dominates up to few MHz, as seen in the other 40.4m systems. Activation energy associated with the temperature dependent of $T_{1//}$ is 7.6 kCal/mol [2]. This value is in agreement with the generally observed activation energy associated with the rotational motion about the molecular short axis [32,33].

Self-Diffusion

The frequency independent contribution from SD extends to higher frequencies in the case of 40.4. The complete profile of the diffusion curve could not be obtained due to the lack of data at high frequencies above 40 MHz in 40.4. The strong temperature dependence of $T_i$ at 39.6 MHz is observed probably due to the domination of SD process at high frequencies. Relaxation in the intermediate frequency region is due to the SD, assisted by DF.
The diffusion constant is $32.4 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$, a higher value comparing with the other 40 m systems, but within the range of the diffusion constants obtained for typical nematic liquid crystals ($0.4 \times 10^5$ to $3 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$) [43].

6.4.2.1.2. Anisotropic elastic constants model

The second method based on the anisotropic elastic constants model gives a slightly different picture of the dynamical parameters. The experimental elastic data given by Tolmachev et al., [30] for 40.4 is used directly in the model fitting for DF. The complete description of the functions and parameters involved in this more generalized model, considering cut-off frequencies as well as anisotropy in the elastic constants have been described in chapter-5, section 5.2. The relative contributions observed from the analysis are depicted in figure 6.18.

Figure 6.18. Proton relaxation rate ($R_i$, $i = 'D'$) as a function of frequency in the nematic phase of 40.4 at 67 °C and model fit (equation 6.1) to three individual contributions to the relaxation rate: director fluctuations (DF), self-diffusion (SD), and molecular reorientations about the short axis (R). Experimental elastic constants are considered in evaluating the DF contribution.
The constant $A_{1/2}$, obtained for 40.4 is $2.2988 \times 10^{-6}$ s$^{-2}$, which is smaller than that of the value obtained from the isotropic elastic constants model. The lower cut-off frequency obtained in this case is 8.8 kHz. The upper cut-off frequencies in the directions parallel and perpendicular to the director are $9 \times 10^8$ Hz and $10 \times 10^8$ Hz, respectively. The DF mechanism contributes effectively to the spin relaxation from 50 kHz to 3 MHz along with R. From 2 MHz onwards, SD become more dominant than DF. The behavior of the NMRD data from 50 kHz to 2 MHz can be attributed to the combined effect of R and DF mechanisms. Above 2 MHz, frequency dependence results from SD and DF. R contribution becomes negligible, from 10 MHz onwards.

The correlation time obtained for rotations about the short molecular axis in the nematic phase of 40.4 from this model is $5.878 \times 10^{-8}$ seconds. The contribution to the total relaxation rate from R is quantified by the value $C = 1.238 \times 10^8$ s$^{-1}$. While the correlation time for rotations show a slight variation, the contribution to the total relaxation increases at the cost of the DF contribution in this model.

In the case of self-diffusion, the values $B$ and $1)$ are obtained as $506 \times 10^9$ s$^{-2}$ and $318 \times 10^{-10}$ m$^2$ s$^{-1}$ respectively. The behavior of the SD contribution is almost the same as that of the previous model. SD shows its frequency behavior at much higher frequencies and hence the NMRD behavior of the nematic phase of 40.4 is characteristic the SD behavior only at high frequencies around 30 MHz.

6.4.2.2. Comparison with the ordered smectic phases

Mechanisms identified for relaxation in N, S$_A$ and S$_i$ phases are different from the mechanisms identified for relaxation in S$_H$, S$_G$ and solid phases. In the N, S$_A$, and S$_C$ phases, the important mechanisms are SD and R about the short axis, along with the nematic DF modes and smectic undulation modes. The negligible discontinuities of $\tau$ in the N-S$_A$ and S$_A$-S$_i$ transition regions and an almost non-discontinuity in the $T_{II}$ values at these transitions supports this view, in contrast with the strong discontinuities found near N-S$_H$, S$_A$-S$_H$ and S$_A$-S$_i$ transitions regions.

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Slowing down of diffusion process and the absence of DF mechanism are responsible for the sudden increase of $\tau$ in the smectic G phase near the $S_{B1} - S_{B1}$ transition, in the conventional NMR frequencies [2]. The increasing nature of $\tau$ in the $S_{B1}$ phase for few degrees is probably attributable due to the decreasing contribution from SD and R, of the whole molecules. A detailed discussion of the data in the smectic B phase in 40.4 is difficult due to the short temperature range of this phase. In the smectic G phase of the 40.4 the $\tau$ data show frequency as well as temperature dependence with the presence of a $\tau$ minimum. The mechanism, probably responsible for the $\tau$ behavior is the rotation of the core, as well as, the segmental motions of the chains. The contribution from the $\text{CH}_3$ rotations of the end chains are not be very efficient [24], when compared to the other two motions (rotations about the long axis and segmental motions) at these temperatures. Since there are two end chains and many $\text{CH}_2$ groups present in the system, several rotational diffusion modes could be present, leading to as many values of the correlation time, possible.
6.5. NMRD study of Butyloxybenzylidene Pentylaniline (40.5)

The system, next studied in 40.m series is butyloxybenzylidenepentylaniline (40.5). This system has the phase sequence given by [7],

\[
\begin{array}{cccccc}
28 \, ^\circ C & 37 \, ^\circ C & 41.5 \, ^\circ C & 44 \, ^\circ C & 82.9 \, ^\circ C \\
X & S_G & S_R & S_A & N & I
\end{array}
\]

A wide and stable nematic (39 °C) phase is seen from 82.9 °C to 44 °C. This highly stable nematic phase seen in the system with fairly symmetric end chains is an interesting point, to be noted.

6.5.7. Experimental Details

Proton spin-lattice relaxation time (7) measurements were carried out as a function of frequency in the nematic phase of 40.5 at temperature 70 °C. The data from 65 kHz to 3 MHz was obtained using the field cycling NMR spectrometer and the high frequency data from 3 to 30 MHz was obtained, using the conventional NMR spectrometer [1]. The estimated errors in 7) measurements at frequencies below 1 MHz are found to be less than 7% and at above 1 MHz, around 5%. This temperature (70 °C) is chosen, since there are no pre-transitional effects found in the temperature dependent 7) data and this temperature is sufficiently away from N-I phase transition. The experimental NMRD data for nematic phase of 40.5 is shown in figure 6.19.

The observed NMRD data in the nematic phase of 40.5 has the following features.

1. The relaxation times ranging from 65 milliseconds at 65 kHz, to 469 milliseconds at 30 MHz, with a decreasing \( T \), with decreasing frequency are observed in the entire frequency range studied.
Figure 6.19. Frequency dependence of the spin-lattice relaxation time ($T_1$) in the nematic phase of 40.5 at temperature 70 °C. Error bars are also shown.

2. $T_1$, in the logarithmic scale shows (figure 6.19) variation as a function of the Larmor frequency with lesser slope in the low frequencies. The slope increases in the intermediate frequencies. At low proton Larmor frequencies, the plot show a very short region having a square-root behavior, indicating the presence of weaker DF contribution. NMRD data deviates from this behavior, from 1 MHz and a sharp variation is observed after this frequency.

3. Thus, the NMRD data in the nematic phase of 40.5 at 70 °C shows at least three different regions with different slopes, and hence, from the first look at the data suggests that there are three possible mechanisms with different frequency dependence.

4. In the conventional NMR region from 4 MHz to 30 MHz, the $T_1$ data in the nematic phase shows an interesting behavior with two different regions. The temperature dependent data at spot frequencies 4, 6.5, 10, 15, 20, 25, and 30 MHz are shown in figure 6.20.
Figure 6.20. The behavior of the spin-lattice relaxation time \( T_1 \) as a function of temperature at different frequencies in 40.5. The arrows denote the transition temperatures

The first region closer to the 1-N phase transition shows an almost constant \( T_1 \) behavior, with decreasing temperature. This trend continues for about 10 °C and another region with strong temperature dependence follows this region at lower temperatures. This second region is seen for about 35 °C, extending up to the nematic to smectic A phase transition. This trend is observed in all frequencies up to 30 MHz. Stronger temperature dependence is seen at higher frequencies.

5. 7) data shows a sudden increase towards higher value at the smectic A to smectic B phase transition and this value increases with a decrease in temperature, finally reaching a maximum value near the \( S_A \) to \( S_B \) phase transition. The data in the highly ordered \( S_B \) and \( S_G \) phases show a strong temperature dependence and weak frequency dependence in the conventional NMR frequency range. The 7) values slightly increases with frequency and strongly decreases with temperature within the frequency in the \( S_B \) and \( S_G \) phases.
6.5.2. Data analysis

6.5.2.1. Nematic Phase

6.5.2.1.1. Isotropic elastic constants model

The frequency dependent relaxation rate \((R - T_f)\) at 70 °C, in the nematic phase of 40.5, was fitted to an equation assuming contributions from all the three dynamic processes, viz., SD, R and DF (equation 6.1). The DF contribution to the NMRD data was fitted in two different ways. The first method is based on the one constant approximation with an assumption that \(K_{11} = K_{22} = K_{33} = 1e^6\) dyne (in this work it is also called as isotropic elastic constants model). The value of \(ADF\) and the lower cut-off frequency were varied to get a good fit. The DF contribution is quantified by the constant \(A_{DF} = 3.47 \times 10^6\) s\(^2\) in the case of the one constant approximation method. The estimation of the upper cut-off frequency becomes difficult in this case. A constant value was given in the model fitting in order to get a good fit. The lower cut-off frequency calculated from the analysis is 24 kHz. and the corresponding upper cut-off wavelength for the director modes is about 24800 Å. The physical significance of the lower cut-off frequency is conflicted in the literature [44] due to the presence of dipolar fields, and hence a correlation of the lower cut-off frequency \(v_{zc}\) with the generally assumed domain size is not simple.

Contributions from various mechanisms to the measured \(R_f\) data are shown in figure 6.21. The dynamic parameters obtained from this model fit are summarized in table 6.4. The uncertainty in determining the model parameters is about 10%. A qualitative picture of the NMRD model fit in the nematic phase of 40.5 reveals that, the DF modes dominate the spin relaxation, at low frequencies upto 6 MHz.

Rotations about the short axis, with a frequency independent behavior from 65 kHz to 300 kHz, and with a frequency dependent behavior upto 1 MHz, contribute to spin relaxation, alongwith the DF. SD becomes more important than R, from about 1 MHz and becomes the most dominating mechanism from 10 MHz. DF and SD
contribute equally at 6.5 MHz, where R has a negligible contribution. At high frequencies SD is solely responsible for relaxation, from about 10 to 30 MHz.

Figure 6.21. Proton relaxation rate ($R_1 / T$) as a function of frequency in the nematic phase of 40.5 at 70 °C and model fit (eqn.6.1) to three individual contributions to the relaxation rate: director fluctuations (DF), self-diffusion (SD), and molecular reorientations about the short axis (R). Isotropic elastic constants model is assumed in evaluating the DF contribution.

From the NMRD data fitting, the percentage contributions of the various dynamical processes at different frequencies can be quantified. For example at 65 kHz, the contribution from DF mechanism to the total relaxation is about 65.5%. The contribution from R and SD are about 23.5% and 10% respectively. At 370 kHz, the contributions from DF, R and SD are about, 52%, 32%, and 16% respectively. This trend continues, and finally R becomes equal to SD and DF at 2.8 MHz. The contributions at 1 MHz are 49% due to DF, 28% due to R and 23% due to SD. The contribution from SD and R becomes equal at 1.2 MHz. At 6.5 MHz, the contribution from R becomes negligible, where SD and DF contributes equally to the spectral density. At the highest measured frequency (30 MHz), DF contribution becomes 32%.
and the remaining 68% relaxation is due to SD mechanism. This analysis is consistent with the strong temperature dependence, characteristic of SD, seen in the $T$, data at higher frequencies.

**Table 6.4**

<table>
<thead>
<tr>
<th>Model Parameters</th>
<th>Isotropic elastic constants model</th>
<th>Anisotropic elastic constants model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nematic director fluctuations (DF)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_{11}$ (in $10^6$ dynes)</td>
<td>1</td>
<td>0.8</td>
</tr>
<tr>
<td>$K_{22}$ (in $10^6$ dynes)</td>
<td>1</td>
<td>0.55</td>
</tr>
<tr>
<td>$K_{33}$ (in $10^6$ dynes)</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td>$A_{DF}$ (in $10^{-6}$ s$^{-2}$)</td>
<td>3.47</td>
<td>2.66</td>
</tr>
<tr>
<td>$q_{zel}$ (in $10^5$ 1/Am)</td>
<td>2.53</td>
<td>1.756</td>
</tr>
<tr>
<td>$f_{zel}$ (in kHz)</td>
<td>24</td>
<td>11.77</td>
</tr>
<tr>
<td>$\lambda_{chal}$ (in A)</td>
<td>2480</td>
<td>3578</td>
</tr>
<tr>
<td>$q_{chal}$ (in $10^7$ 1/Am)</td>
<td>6.8</td>
<td>3.024</td>
</tr>
<tr>
<td>$f_{chal}$ (in MHz)</td>
<td>1400</td>
<td>349</td>
</tr>
<tr>
<td>$\lambda_{cl}$ (in A)</td>
<td>9.24</td>
<td>20.77</td>
</tr>
<tr>
<td>$q_{cl}$ (in $10^7$ 1/Am)</td>
<td>6.4</td>
<td>5.4</td>
</tr>
<tr>
<td>$f_{cl}$ (in MHz)</td>
<td>1300</td>
<td>930</td>
</tr>
<tr>
<td>$\lambda_{cl}$ (in A)</td>
<td>9.81</td>
<td>11.6</td>
</tr>
<tr>
<td>Translational self-diffusion (SD)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B$ (in $10^9$ s$^{-2}$)</td>
<td>456.6</td>
<td>444.8</td>
</tr>
<tr>
<td>$D$ (in $10^{-10}$ m$^2$ s$^{-1}$)</td>
<td>363.1</td>
<td>349.6</td>
</tr>
<tr>
<td>Rotations about the short axis (R)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$'$(in $10^8$ s$^{-2}$)</td>
<td>0.45</td>
<td>0.482</td>
</tr>
<tr>
<td>$\tau_R$ (in $10^9$ s)</td>
<td>82.1</td>
<td>64.1</td>
</tr>
</tbody>
</table>
Reorientations about the short molecular axis

The correlation time obtained for rotations about the short molecular axis in the nematic phase of 40.5 is $8.21 \times 10^{-8}$ seconds. Contribution to the total relaxation rate from $R$ is quantified by the value $C = 4.5 \times 10^7 \text{ s}^{-1}$.

Self-Diffusion

In the case of self-diffusion, the model parameter $B$ (the amplitude) is equal to $4.566 \times 10^{-11} \text{ s}^2$, and $D$ (the average diffusion constant) is equal to $36.3 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$. The frequency independent contribution from SD extends to higher frequencies in 40.5. The complete profile of the diffusion curve could not be obtained due to lack of data at high frequencies, above 30 MHz. The diffusion constant obtained in this case is higher than the $D$ value obtained from direct methods. One probable reason for such a difference (about an order of magnitude) is probably due to the non-availability of the NMRD data in the region of frequencies, where one can see the complete dispersion of SD.

6.5.2.1.2. Anisotropic elastic constants model

The second method, with the anisotropic elastic constants ($K_{11} = 0.8 \times 10^{-6}$, $K_{22} = 0.55 \times 10^{-6}$, and $K_{33} = 1.2 \times 10^{-6}$ dyne) model for DF contribution gives a slightly different picture. The model fit is shown in figure 6.22. The elastic constants are calculated by extrapolating experimental data for 40.4 [30]. The details of the calculation of the elastic constants have been given at the beginning of the chapter (section 6.1). The constant $A_{DF}$ obtained for 40.5 is $2.6597 \times 10^{-6} \text{ s}^{-2}$, which is smaller than the value obtained from the one constant approximation model. The lower cut-off frequency in this case is 11.7 kHz. The upper cut-off frequencies in the directions parallel and perpendicular to the director are $3.5 \times 10^8$ Hz and $9.3 \times 10^8$ Hz, respectively. The parameters obtained from both these methods are given in table 6.4.
Figure. 6.22. Proton relaxation rate ($R_i - 1/T_i$) as a function of frequency in the nematic phase of 40.5 at 70 °C and model fit (eqn. 6.1) to three individual contributions to the relaxation rate: director fluctuations (DF), self-diffusion (SD), and molecular reorientations about the short axis (R). Anisotropic elastic constants model is considered for DF contribution.

The correlation time obtained for rotations about the short molecular axis in the nematic phase of 40.5 is $8.21 \times 10^{-8}$ seconds. The contribution to the total relaxation rate from R is quantified by the value $\tau = 4.5 \times 10^7$ s$^{-1}$. The correlation time changes slightly when comparing with the earlier analysis. In the case of self-diffusion, the model parameter $B$ is equal to $4.566 \times 10^{11}$ s$^{-2}$, and $D$, the average diffusion constant is equal to $36.3 \times 10^{-5}$ m$^2$ s$^{-1}$. Diffusion parameters ($B$ and $D$) obtained with the anisotropic elastic constants model for DF modes are almost the same as that of the parameters obtained in the case of the isotropic elastic constants model.
6.5.2.2 Smectic A phase

NMRD data measured in the smectic A phase from 65 kHz to 30 MHz, is shown in figure 6.23. This data was fitted with the theoretical equation incorporating three dynamical processes namely, the smectic layer undulation modes (LU), SD and R. Thus, the spin-lattice relaxation rate \( R_{1\text{LA}} \) in the \( S_A \) phase can be written as

\[
R_{1\text{LA}} = R_{1LU} + R_{1\text{SD}} + R_{1R}
\]

where \( R_{1\text{LU}} \) given by equation 6.3, represents the contribution to total \( R_1 \), from the smectic layer undulation modes. Different contributions to the relaxation rate in the smectic A phase of 40.5 shown in figure 6.24.

![Figure 6.23. Frequency dependence of the spin-lattice relaxation time (7;) in the smectic A phase of 40.5 at temperature 43 °C. Error bars are also shown in figure.](image)

LU contribution in the smectic A phase is dominant, only upto 200 kHz, in 40.5. Diffusion becomes more important, and strongly contributes to relaxation in the \( S_A \) phase of 40.5. SD contribution is almost frequency independent upto 10 MHz. \( R \) also contributes to the relaxation rate, till about a few MHz. From 6.5 MHz, SD mediates the relaxation completely, where \( R \) and DF become negligible.

275
Figure 6.24. Proton relaxation rate \( R/T_i \) as a function of frequency in the smectic A phase of 40.5 at 43 °C and model fit (eqn. 6.4) to three individual contributions to the relaxation rate: layer undulations (LU), self-diffusion (SD), and molecular reorientations about the short axis (R).

The \( T_{iD} \) data in the smectic A phase [1] shows temperature dependence. This is qualitatively different from the \( T_{iH} \) data obtained form the higher homologous 40.6, 40.7 and 40.9, where \( T_{iH} \) data in the \( S_A \) phase are almost temperature independent. The strong SD contribution in the \( S_A \) phase of 40.5 at low frequencies as observed in the present analysis is consistent with the temperature dependent \( T_{iD} \) behavior. The model parameters obtained for SD and R about the short axis in the \( S_A \) phase are given in the table 6.5. The parameters for LU are not presented here due to the large uncertainty in evaluating them in the present NMRD frequency range. It is known that [11,48,51] LU mechanism strongly contributes at lower frequencies, where the \( T_1 \) data was not collected due to the experimental limitations. The estimated errors in the evaluation of the dynamic parameters for SD and R are around 10%.
Table 6.5.

<table>
<thead>
<tr>
<th>Translational self-diffusion (SD)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$B \ ( \text{in} \ 10^{9} \ s^{-2})$</td>
<td>1.14</td>
</tr>
<tr>
<td>$D \ ( \text{in} \ 10^{\frac{n}{10}} \ m^2s^{-1})$</td>
<td>2.1753</td>
</tr>
<tr>
<td>Rotations about the short axis (R)</td>
<td></td>
</tr>
<tr>
<td>$C^* \ ( \text{in} \ 10^{8} \ s^{-2})$</td>
<td>0.91</td>
</tr>
<tr>
<td>$TR \ (\text{in} \ 10^{3} \ s)$</td>
<td>4.1644</td>
</tr>
</tbody>
</table>

6.5.2.3. *Ordered smectic Phases*

The NMRD data obtained in the case of 40.5 smectic B phase is shown in figure 6.25. NMRD data is fitted to SD and R mechanisms, as shown in figure 6.26. The models used in the evaluation of the contributions from SD and reorientations are presented in the chapter 5.

![Figure 6.25 Frequency dependence of the spin-lattice relaxation time ($T_1$) in the smectic B phase of 40.5 at temperature 40 °C. Error bars are also shown.](image)
Figure 6.26. Proton relaxation rate \((R/\tau_i)\) as a function of frequency in the smectic B phase of 40.5 at 40 °C and model fit to the individual contributions to the relaxation rate: self-diffusion (SD), and molecular reorientations (R).

Table 6.6

<table>
<thead>
<tr>
<th>Model Parameters</th>
<th>From 4O.5-S_B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B) (in (10^V))</td>
<td>1.4056</td>
</tr>
<tr>
<td>(D) (in (10^{-13} \text{ m}^2\text{s}^{-1}))</td>
<td>2.412</td>
</tr>
<tr>
<td>(C^*) (in (10^9 \text{ s}^{-1}))</td>
<td>4.659</td>
</tr>
<tr>
<td>(\tau_R) (in (10^{16} \text{ s}))</td>
<td>6.055</td>
</tr>
</tbody>
</table>

The low frequency region is completely dominated by the SD mechanism and the higher frequency relaxation, by rotations. This interpretation is consistent with the observations made with the temperature dependent data [2]. In the highly ordered smectic B phase, the diffusion constant becomes very small \((D = 2.41 \times 10^{-9} \text{ cm}^2/\text{s})\) and relaxation dispersion is explained by the SD process. A relatively small, frequency independent contribution comes from R at low frequencies. The strong temperature
dependence seen in the high frequency $\tau_7$ data is consistent with this view. The temperature dependence of $T_{1//}$ at these temperatures represents the SD mechanism. The explanation given for the $T_{1//}$ data for the $S_R$ phase is also consistent with the NMRD analysis. The dynamic parameters are given in table 6.6. Typical errors in estimating the dynamic parameters in this case is about 15%.

Rotations in the ordered smectic ($S_R$ and $S_i$) phases can be best described using three different rotational dynamic processes generally present in the chain molecules [24]. The observations made by earlier studies [24] that have been described in the introductory section of this chapter (section 6.1), are useful in understanding the contributions of various dynamic processes to $\tau_7$ and $T_{1//}$ in the ordered smectic phases and also in the solid phases. The sudden increase of $\tau_7$, observed near the transition from smectic A to smectic B in both $T_{1//}$ and $\tau_7$ at frequencies between 5-30 MHz clearly demonstrates the basic difference between the dynamic properties of highly ordered smectic phases and the fluid like nematic and smectic A phases. Slowing down of the diffusion process and the absence of the DF mechanism are responsible for the sudden increase of $\tau_7$ in the smectic G phase near the SB-SG transition, in the conventional NMR frequencies. In the smectic B and smectic G phases of the 40.5, the $\tau_7$ data shows a weak frequency dependence and strong temperature dependence.

The probable mechanisms responsible for the $R_{1//}$ behavior shown in the NMRD data analysis are due to the rotation of the core, to a large extent and due to the segmental motions of the chains. In 40.5, anisotropic rotational diffusion motions of the end hydrocarbon chains, of the entire molecule, or of just the core rigid portions, are possible at these temperatures. From the behavior of the data in the $S_R$ and $S_G$ phases at the measured temperature ranges, it can be concluded that, the major contribution is from the rotations of the molecule around the long axis and from the segmental motions.
6.6. NMRD study of Butyloxybenzylidene Heptylaniline (40.7)

The next system, studied in the \(40.\)\(m\) series is *butyloxybenzylidene heptylaniline* (40.7). This system has the phase sequence given by \[7\],

\[
\begin{array}{cccccc}
-20^\circ C & 49^\circ C & 50^\circ C & 57^\circ C & 83^\circ C \\
X & \cdots & S_B & S_C & S_A & N & I
\end{array}
\]

A stable and wide nematic phase (26 \(^\circ\)C) seen from 83 \(^\circ\)C to 57 \(^\circ\)C and a smectic A phase with a temperature range of about 7 \(^\circ\)C is observed in 40.7. A smectic C phase of about 1 \(^\circ\)C along with a very wide \(S_B\) phase ranges from 49 \(^\circ\)C to -20 \(^\circ\)C were also seen.

**6.6.1. Experimental Details**

Proton spin-lattice relaxation time (\(T_1\)) measurements were carried out as a function of frequency in the nematic phase of 40.7, at a temperature of 75 \(^\circ\)C. The data from 50 kHz to 3 MHz was obtained using the field-cycling NMR spectrometer, and the high frequency data from 3 to 30 MHz were obtained using the conventional NMR spectrometer \[1\]. The estimated errors in \(T_1\) measurements at frequencies below 1 MHz are found to be less than 7% and at above 1 MHz, around 5%.

Experimental NMRD data for nematic phase are shown in figure 6.27. The temperature dependent data at spot frequencies at 6.5, 10, 15, 20, and 30 MHz are shown in figure 6.28. The observed NMRD data in the nematic phase of 40.7 has the following features.

1. The relaxation times range from 49.5 milliseconds at 50 kHz to 480 milliseconds at 30 MHz
Figure 6.27. Frequency dependence of the spin-lattice relaxation time ($T_1$) in the nematic phase of 40.7 at temperature 75 °C. Error bars are also shown.

Figure 6.28 The behavior of the spin-lattice relaxation time ($T_1$) as a function of temperature at different frequencies in 40.7. The arrows denote the transition temperatures
2. $T_2$ in the logarithmic scale (figure 6.28) shows a steep variation as a function of the Larmor frequency at low frequencies, from 50 kHz to 1 MHz. The slope increases in the intermediate frequencies (from 1 MHz to 10 MHz) and finally reaches another region with lesser slope at higher frequencies (10 to 30 MHz). The plot between relaxation rate and frequency (in Hz) at low proton Larmor frequencies, show a slightly longer region having a square-root like behavior, indicating the presence of a longer region with DF mechanism. The NMRD data deviates from this behavior, from about 2 MHz.

3. Thus NMRD data in the nematic phase of 40.7 at 75°C shows at least two different regions with different slopes, and hence a first glance at the data suggests that there are at least two possible mechanisms with different frequency dependencies.

4. In the conventional NMR region from 6.5 MHz to 30 MHz, the $T_2$ data shows an interesting behavior with two different regions. The first region close to the I-N phase transition show, almost a constant $T_2$ value with decreasing temperature. This trend continues for about 10°C and the second region with strong temperature dependence is seen below this temperature range. This region continues for about 16°C extending upto the nematic to smectic A phase transition. The temperature independent region decreases with increasing frequency.

5. NMRD data in the smectic A phase shows three regions with different slopes. The first region (though very short) with steep behavior is seen below 150 kHz. The second region with a lesser slope is observed from 200 kHz to 6.5 MHz and finally, it reaches a different region with very weak frequency dependence above 6.5 MHz.

6. This behavior indicates the presence of three mechanisms. The short region having a very high slope is probably due to the LU mechanism. The observed continuity between the nematic and smectic A phase (in the temperature dependent $T_1$ data) suggests that there are common mechanisms, which influence spin relaxation in the conventional NMR frequencies. The $T_1$ in the smectic A phase shows strong temperature dependence. This behavior is almost similar, at all the frequencies.
7. A sudden increase towards higher value of $l$ at the smectic A to Smectic B phase transition is seen in the data and this value increases with decreasing temperature. The data in the ordered $S_{B}$ phase shows strong temperature dependence and weak frequency dependence in the conventional NMR frequency range.

### 6.6.2. Data analysis

#### 6.6.2.1. Nematic Phase

##### 6.6.2.1.1. Isotropic elastic constants model

It is important to introduce the contribution from the rotation about the short molecular axis (R), along with the SD and DF in the analysis in order to explain the intermediate frequency range from a few hundred kHz to a few MHz. Similarly, the low frequency cut-off is necessary to fit the low frequency data at kHz range satisfactorily. So, the frequency dependent relaxation rates ($R_{1''}$) at 75 °C in the nematic phase of 40.7 were fitted to the following equation assuming a contribution from all the three dynamic processes, viz., SD, R and DF.

$$R_{1''_{tot}} = R_{1''_{DF}} + R_{1''_{SD}} + R_{1''_{R}}$$

The value of $A_{DF}$ and the cut-off frequencies were varied to get good fit. The DF contribution is quantified by the constant $ADF = 3.457 \times 10^6 \text{ s}^{-2}$ in the case of the one constant approximation method. The lower cut-off frequency is about 18 kHz, and the corresponding upper cut-off wavelength for the director modes is 39800 Å.

**Relative contributions**

The contributions from various mechanisms to the measured $R_{I}$ data are shown in figure 6.29. The dynamic parameters obtained from this fit are summarized in table 6.7. The uncertainty in obtaining the dynamic parameters is found to be about 10%. A qualitative picture of the fit in the nematic phase of 40.7 reveals that the DF
modes dominate the spin relaxation up to 6 MHz. R about the short axis with frequency independent behavior from 50 kHz to 1 MHz and with a frequency dependent behavior up to 3 MHz, contributes to spin relaxation along with the DF and SD. SD becomes more important than R, from about 2.2 MHz and becomes the most dominant mechanism, from 7 MHz. DF and SD contribute equally at 7 MHz, where R has a negligible contribution. At high frequencies SD is the dominating mechanism over DF for relaxation, from 20 to 30 MHz.

![Proton relaxation rate](image)

Figure 6.29. Proton relaxation rate ($R_i - 1/T_i$) as a function of frequency in the nematic phase of 4O.7 at 70 °C and model fit to three individual contributions to the relaxation rate: director fluctuations (DF), self-diffusion (SD), and molecular reorientations about the short axis (R). Isotropic elastic constants are assumed in evaluating the DF contribution.
A more quantitative picture of the relative contributions can be obtained by calculating the percentage contribution due to various mechanisms. For example at 50 kHz, the contribution from DF mechanism to the total relaxation is about 65.5%. The contributions from R and SD are about 23.5% and 10% respectively. At 370 kHz, the contributions from DF, R and SD are about, 52%, 32%, and 16% respectively.
This trend continues, and finally R becomes equal to SD and DF at 2.8 MHz. The contributions at 1 MHz are 49% due to DF, 28% due to R and 23% due to SD. The contributions from SD and R become equal at 1.2 MHz. At 6.5 MHz, the contribution from R becomes negligible, where SD and DF contributes equally to the spectral density. At the highest measured frequency (30 MHz) the DF contribution becomes 32% and the remaining 68% relaxation is almost due to SD mechanism. This view is consistent with the strong temperature dependence expected for SD of the $T_1$ data.

The correlation time obtained for rotations about the short molecular axis in the nematic phase of 40.7 is $3.389 \times 10^{-8}$ seconds. The contribution to the total relaxation rate from R is quantified by the value $C = 9.124 \times 10^7 \text{ s}^{-1}$. Presence of strong contribution from DF modes in the nematic phase at low frequencies in the kHz region lead to the temperature dependent dipolar relaxation times ($T_{1D}$) [1].

In the case of self-diffusion, the model parameters are $B$ (the amplitude obtained as $6.38 \times 10^9 \text{ s}^2$), and $D$ (the average diffusion constant obtained as $5.07 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$). The strong temperature dependence at high frequency data observed is due to the presence of SD process at high frequencies.

6.6.2.1.2. Anisotropic elastic constants

The complete description of the functions and parameters are involved in this generalized model (called anisotropic elastic constants model) have been described in chapter 5. The experimental elastic data given by Tolmachev et al., [30] for 40.4 is deduced, keeping the general trends followed by other homologous series of nematic liquid crystals in mind, in order to obtain elastic constants for the 40.7 system. NMRD fitting with anisotropic elastic constants is shown in figure 6.30. In this model the $A_{DF}$ value obtained is $1.38 \times 10^{-6} \text{ s}^2$ which is lesser compared to the value obtained from the isotropic elastic constant model. The lower cut-off frequency in this case is 3.15 kHz, which is smaller than the value obtained from the one constant elastic constants model. Model fitting is better in the case of the anisotropic elastic constants model.
Figure 6.30. Proton relaxation rate \( R_1 \) as a function of frequency in the nematic phase of 40.7 at 70 °C and model fit to three individual contributions to the relaxation rate: director fluctuations (DF), self-diffusion (SD), and molecular reorientations about the short axis (R). Anisotropic elastic constants model is considered for DF contribution.

The correlation time obtained for rotations about the short molecular axis in the nematic phase of 40.7 is \( 3.73 \times 10^{-9} \) seconds. The contribution to the total relaxation rate from R is quantified by the value \( C = 48.4 \times 10^9 \) s\(^{-1}\). In the case of self-diffusion, the model parameter \( B \) is equal to \( 44.48 \times 10^{10} \) s\(^{-2}\) and \( J \), the average diffusion constant is equal to \( 349.6 \times 10^{-10} \) m\(^2\) s\(^{-1}\). Diffusion parameters (\( B \) and \( D \)) obtained with the anisotropic elastic constants model for DF modes are very different from the parameters obtained in the case of the isotropic elastic constants model.

DF mechanism dominates spin relaxation from 50 kHz to 1 MHz, where the contribution from the R frequency independent. From 1 MHz, R and DF contribute equally and this explains the slight deviation in the experimental NMRD data from 1 MHz to 3 MHz. From 3 MHz onwards, SD contribution becomes comparable with the DF contribution. From 3 to 4 MHz, all the three mechanisms contribute almost equally. R loses its important from 7 MHz. SD becomes the most dominating
mechanism from 4 MHz onwards. DF contribution becomes very less from 20 MHz where SD is responsible for the frequency dependence in the NMRD data. Percentage contributions can be calculated from this fitting.

6.6.2.2. Smectic A phase

The NMRD data collected in the smectic A phase (figure 6.31) was fitted with the theoretical equation incorporating the three dynamical processes namely 1. Smectic layer undulation modes (LU), 2. SD and 3. Rotations about the short axis. The details of the theoretical formalism are given in chapter-5.

Each of these contributions has characteristic frequency and temperature dependencies, which have already been discussed, in the introductory section. Different contributions to the relaxation rate are shown in figure 6.32

![Graph showing T1 (ms) vs Frequency (Hz)](image)

Figure 6.31. Frequency dependence of the spin-lattice relaxation time (T1) in the smectic A phase of 40.7 at temperature 54 °C. Errors bars are also shown.
Figure 6.32. Proton relaxation rate ($R_i$) as a function of frequency in the smectic A phase of 40.7 at 54 °C and model fit (equation 6.4) to three individual contributions to the relaxation rate: layer undulations (LU), self-diffusion (SD), and molecular reorientations about the short axis (R).

The parameters are given in table 6.8. LU contribution in the smectic A phase is dominant up to 150 kHz in 40.5. The dynamic parameters related to the LU mechanism are not given keeping the large uncertainties in evaluating the values in the present frequency range where LU contribution is very weak. The dynamic parameters are obtained within the error limit of about 10% in this case also.

R becomes more important from 150 kHz to 2 MHz in this case and strongly contributes to the relaxation in the $S_A$ phase of 40.7. From 6.5 MHz, SD mediates the relaxation completely where R and LU becomes negligible. SD contribution is almost frequency independent up to 3 MHz. The $T_{1D}$ data in smectic A phase shows temperature independence. This is qualitatively different from the $T_{1H}$ data obtained from the other homologue 40.5, where $T_{1H}$ data, is in the $S_A$ phase is almost
temperature dependent. Weak contribution of SD in the $S_A$ phase of 40.7 at low frequencies is consistent with the temperature independent $T_{1\parallel}$ behavior.

Table 6.8

<table>
<thead>
<tr>
<th>Translational self-diffusion (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$ ($10^9$ s$^{-2}$)</td>
</tr>
<tr>
<td>$D$ ($10^{-11}$ m$^2$ s$^{-1}$)</td>
</tr>
</tbody>
</table>

Rotations about the short axis (R)

| $C$ ($10^8$ s$^{-1}$) | 1.826 |
| $\tau_R$ ($10^8$ s)   | 4.549 |

6.6.2.3. Comparison with the ordered smectic phase

The observations made in the literature [24] which have been described in the introductory section of this chapter, are useful in understanding the contributions of various dynamic processes to $\tau \bot$ and $T_{1\parallel}$ in the highly ordered smectic B phases. The observed increase of $\tau \bot$ at the transition from smectic A to smectic B in both $T_{1\parallel}$ and $\tau$ at frequencies between 5-30 MHz clearly demonstrates the difference between the dynamic properties of highly ordered smectic phases and the fluid like nematic and smectic A phases.

Slowing down of diffusion process and the absence of the DF/LU mechanism are responsible for the sudden increase of $T_i$ in the smectic B near the $S_A-S_H$ transition, in the conventional NMR frequencies. In the smectic B phase of the 40.7 the $T_i$ data shows strong temperature dependence. The probable mechanisms responsible for the $T_i$ behavior shown in the data are the rotation of the core, and due to the segmental motions of the chains. From the behavior of the data in the $S_H$ phase at the measured temperature ranges, it can be concluded that, the major contribution comes from the rotations of the molecule around the long axis and from the segmental motions.
6.7. NMRD study of Butyloxybenzylidene Octylaniline (4O.8)

The next system under study in the 40.m series is butyloxybenzylidene octylaniline (40.8). This system has the phase sequence given by [7],

\[
\begin{array}{cccc}
33^\circ C & 49.5^\circ C & 64.5^\circ C & 79^\circ C \\
X & S & S & N
\end{array}
\]

6.7.7. Experimental Details

Proton spin-lattice relaxation time (T1) measurements were carried out as a function of the Larmor frequency in the nematic phase of 40.8 at temperature 71 °C. The NMRD data from 50 kHz to 3 MHz was obtained using the field cycling NMR spectrometer and the high frequency data from 3 to 45 MHz was obtained using the conventional NMR spectrometer. The estimated errors in T1 measurements at frequencies below 2 MHz found to be less than 7% and at above 2 MHz, around 5%.

Figure 6.33. Frequency dependence of the spin-lattice relaxation time (T1) in the nematic phase of 40.8 at temperature 71 °C. Error bars are also shown.
The experimental NMRD data is shown for the \textit{nematic} phase in figure.6.33. The observed NMRD data in the nematic phase of 40.8 has very interesting features. The relaxation times range from 38 milliseconds at 50 kHz to 400 milliseconds at 40 MHz. $T_i$ in the logarithmic scale shows a steep variation as a function of Larmor frequency at low frequencies, from 50 kHz to 300 kHz. The slope decreases in the intermediate frequencies (from 400 kHz to 900 kHz). Another region with increased slope at the intermediate frequency range from 1 to 10 MHz is seen, which is followed by a region with very small variation from 10 to 45 MHz. Thus, the NMRD data show four different regions, indicating the presence of three different processes with different frequency dependencies.

At low proton Larmor frequencies, the NMRD data show a region having square-root behavior indicating the presence of stronger DF mechanism at this frequency range. The NMRD data deviates from this behavior from about 500 kHz and a slight slope change follows this region indicating the presence of another mechanism along with DF.

\section*{6.7.2. Data analysis}

\subsection*{6.7.2.1. Nematic Phase}

\subsubsection*{6.7.2.1.1. Isotropic elastic constants model}

The frequency dependent relaxation rate ($R = 1/T_i$) at 68 °C in the nematic phase of 40.8 was fitted to an equation assuming contributions from all the three dynamic processes, viz., SD, R and DF. The total spin lattice relaxation rate ($R_{\text{Tot}}$) can be written as

$$R_{\text{Tot}} = R_{\text{DF}} + R_{\text{SD}} + R_{\text{R}}$$

In 40.8 the DF contribution to the NMRD data was fitted in two different ways. The first method is based on the one constant approximation ($K_{11}$, $K_{22}$, $K_{33} = 1 \times 10^6$ dyne). The value of $A_{DF}$ and the cut-off frequencies were varied to get a good fit.
The DF contribution is quantified by the constant $A_{DF} = 4.14 \times 10^6 \text{ s}^{-2}$ in the case of one the constant approximation method. The lower cut-off frequency is about 860 Hz, and the corresponding upper cut-off wavelength for the director modes is about 12000 A.

Figure 6.34. Proton relaxation rate ($R_i = 1/T_i$) as a function of frequency in the nematic phase of 40.8 at 71 °C and model fit to three individual contributions to the relaxation rate: director fluctuations (DF), self-diffusion (SD), and molecular reorientations about the short axis (R). Isotropic elastic constants model is assumed for DF contribution.

Upper cut-off frequencies and other dynamic parameters are given in table 6.9. The errors estimated in evaluating the dynamic parameters are about 10 %. The contributions from various mechanisms to the measured $R_i$ data are shown in figure 6.34. A qualitative picture of the fit in the nematic phase of 40.8 reveals that the DF modes dominate the spin relaxation at low frequencies which extend upto 5.7 MHz. R about the short axis with a frequency independent behavior from 50 kHz to 800 kHz and with a frequency dependent behavior upto 10 MHz contributes to the spin relaxation along with the DF. Frequency independent SD becomes more important than R, from about 1 MHz and becomes the most dominating mechanism from 5.7 MHz. DF and SD contribute equally at 5.7 MHz.
contribution. At high frequencies SD and DF contributes to the spin relaxation from 15 to 30 MHz. This interpretation is supported also by the weak temperature dependence of the $T_s$ data at high NMR frequencies.

### Table 6.9

<table>
<thead>
<tr>
<th>Model Parameters</th>
<th>Isotropic elastic constants model</th>
<th>Anisotropic elastic constants model</th>
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<tbody>
<tr>
<td>Nematic director fluctuations (DF)</td>
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<tr>
<td>$K_{11}$ (in $10^{-6}$ dynes)</td>
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<tr>
<td>$K_{22}$ (in $10^{-6}$ dynes)</td>
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<tr>
<td>$K_{33}$ (in $10^{-6}$ dynes)</td>
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<td>$A_{DF}$ (in $10^{-6}$ s$^2$)</td>
<td>4.639</td>
<td>2.026</td>
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<tr>
<td>$q_{zcl}$ (in $10^5$ l/Am)</td>
<td>0.94</td>
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<td>$f_{zcl}$ (in kHz)</td>
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<td>$\lambda_{zcl}$ (in A)</td>
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<td>$f_{zch}$ (in MHz)</td>
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<td>$\lambda_{zch}$ (in A)</td>
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<td>11.4</td>
</tr>
<tr>
<td>$q_{lch}$ (in $10^7$ l/Am)</td>
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<td>6.8</td>
</tr>
<tr>
<td>$f_{lch}$ (in MHz)</td>
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<td>1470</td>
</tr>
<tr>
<td>$\lambda_{lch}$ (in A)</td>
<td>9.81</td>
<td>9.24</td>
</tr>
<tr>
<td>Translational self-diffusion (SD)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B$ (in $10^9$ s$^{-2}$)</td>
<td>1.516</td>
<td>3.256</td>
</tr>
<tr>
<td>$D$ (in $10^{-10}$ m$^2$ s$^{-1}$)</td>
<td>0.7122</td>
<td>1.642</td>
</tr>
<tr>
<td>Rotations about the short axis (R)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C$ (in $10^8$ s$^{-2}$)</td>
<td>0.70</td>
<td>0.9797</td>
</tr>
<tr>
<td>$\tau_R$ (in $10^{-9}$ s)</td>
<td>44.37</td>
<td>39.55</td>
</tr>
</tbody>
</table>
A more quantitative picture of the relative contributions can be obtained by calculating the percentage contribution due to various mechanisms. For example at 50 kHz, the contribution from DF mechanism to the total relaxation is about 76.5% and the contribution from R and SD are about 14.4% and 9.1% respectively. At 200 kHz, the contributions from DF, R and SD are about 63.4%, 22.4%, and 14.2% respectively. At 600 kHz DF contributes about 51.7% and R and SD contributes 28.9% and 19.32% respectively. This trend continues, and finally R becomes equal to SD at 1.8 MHz. The contributions at 2 MHz are 43.8% due to DF, 26.8% due to R and 29.4% due to SD. The contributions from SD and DF become equal at 4.8 MHz. At 10 MHz, the contribution from R becomes very less and the contributions are 38.6%, 55.8% and 5.5% from DF, SD and R, respectively. At the highest measured frequency (40 MHz) DF contribution becomes 27% and about 72.5% relaxation caused by the SD mechanism. R contribution is (0.5%) negligible.

The correlation time obtained for rotations about the short molecular axis in the nematic phase of 40.8 is $3.958 \times 10^{-8}$ seconds. The contribution to the total relaxation rate from R is quantified by the value $C = 9.8 \times 10^7$ s$^{-1}$. Presence of a smaller contribution from rotations about the short axis and the strong DF contribution in the kHz region leads to the temperature independent dipolar relaxation times ($\tau_{dd}$) [45]. In the case of self-diffusion, the model parameters obtained are $B$ (the amplitude obtained as $3.05 \times 10^9$ s$^{-2}$), and $D$ (the average diffusion constant obtained as $1.56 \times 10^{-6}$ m$^2$ s$^{-1}$)

6.7.2.1.2. Anisotropic elastic constants

In the second procedure an expression, considering the influence of upper and lower cut-off wavelengths for the director modes, as well as the anisotropy in elastic properties, was used in calculating the DF parameters. Complete description of the functions and parameters involved in this generalized model have been described in chapter 5. section 5.2.
The elastic constants are calculated by extrapolating experimental elastic data [30] obtained in the nematic system 40.4 at different temperatures. The constant $A_{DF}$ obtained for 40.8 is $2.026 \times 10^6$ s$^{-2}$, which is much smaller than that of the value obtained from the isotropic elastic constants model. The lower cut-off frequency obtained in this case is 589 Hz. The upper cut-off frequencies in the directions parallel and perpendicular to the director are $8.82 \times 10^8$ Hz and $14.7 \times 10^8$ Hz, respectively. The relative contributions observed from the analysis are depicted in figure 6.35.

![Figure 6.35. Proton relaxation rate ($R_1 - iT_1$) as a function of frequency in the nematic phase of 40.8 at 71 °C and model fit to three individual contributions to the relaxation rate: director fluctuations (DF), self-diffusion (SD), and molecular reorientations about the short axis (R). Anisotropic elastic constants model is considered for DF contribution.](image)

DF mechanism dominates the spin relaxation from 50 kHz to 4 MHz, where DF becomes equal to the SD contribution. From 15 MHz onwards, SD becomes more dominant. At 45 MHz the percentage contributions are 25% and 75% due to DF and
SD, respectively The behavior of the NMRD data from 600 kHz to 2 MHz arises from the combined effect of SD and R mechanisms. Below 600 kHz the frequency dependence is due to the DF alone. R and SD contribute to the relaxation with a frequency independent behavior below 600 kHz. R contribution becomes negligible from 8 MHz onwards Model fitting in the nematic phase of 40.8, becomes better in the case of anisotropic elastic constant model. From 5.7 to 20 MHz, SD and DF contributions mediates relaxation, where SD contribution is dominant. SD becomes the major mechanism above 20 MHz The SD contribution from 50 kHz to 10 MHz is almost frequency independent, and it becomes frequency dependent from 10 to 45 MHz

The correlation time obtained for rotations about the short molecular axis in the nematic phase of 40.8 in this model is $3.95 \times 10^{-8}$ seconds. The contribution to the total relaxation rate from R is quantified by the value $\tau = 9.7 \times 10^7$ s$^{-1}$. While the correlation time for rotations show a slight variation; the contribution to the total relaxation increases considerably at the cost of the DF contribution in this model. In the case of self-diffusion, the values $B$ and $D$ are obtained as $3.256 \times 10^{-9}$ s$^{-2}$ and $1.642 \times 10^{-10}$ m$^2$ s$^{-1}$ respectively. The behavior of the SD contribution is not very different from the earlier analysis though SD shows its frequency dependence at much lower frequencies Though there are some differences in the quantitative picture, the qualitative picture of the dynamics are not very different, with the type of approximation (one constant or anisotropic elastic constants model) used The value of $A_{\text{DF}}$ is found to be very sensitive to the anisotropy of the elastic constants.
6.8. NMRD study of Butyloxybenzylidene Nonylaniline (40.9)

The system studied next in the 40.m series is *butyloxybenzylidene nonylaniline* (40.9). This system has the phase sequence given by [7]

\[
\begin{array}{cccc}
<30°C & 47°C & 64.7°C & 80.2°C \\
X & S_\alpha & S & N \uparrow
\end{array}
\]

This system has a stable smectic A phase over a region of 17.7 °C along with a reasonably stable high temperature nematic phase of 15.5 °C.

### 6.8.1. Experimental Details

Proton spin-lattice relaxation time \((T_1)\) measurements were carried out as a function of frequency in the nematic phase of 40.9 at temperature 75 °C. The data from 50 kHz to 3 MHz was obtained using the field cycling NMR spectrometer and the high frequency data from 3 to 30 MHz was obtained using the NMR spectrometer [1]. The estimated errors in \(T_1\) measurements at frequencies below 1 MHz are found to be less than 7 % and at above 1 MHz, around 5 %. Temperature dependent \(T_1\) and \(T_{1D}\) in the nematic and smectic phases were performed earlier in this laboratory [1]. Experimental NMRD data are shown for nematic phase of 40.9 in figure 6.36. Temperature dependent \(T_1\) data at spot frequencies at 6.5, 10, 15, 20, 25, 30, 40 and 45 MHz are shown in figure 6.37. The observed NMRD data in the nematic phase of 40.9 has the following features.

1. The relaxation times ranging from 32 milliseconds at 50 kHz to 502 milliseconds at 45 MHz. \(T_1\) decrease with decreasing frequency in the entire frequency range studied.
Figure 6.36. Frequency dependence of the spin-lattice relaxation time ($T_1$) in the nematic phase of 40.9 at temperature 75 °C. Error bars are also shown.

Figure 6.37. The behavior of the spin-lattice relaxation time $T_1$ as a function of temperature at different frequencies in 40.9. The arrows denote the transition temperatures.
2. In the logarithmic scale shows a steep variation as a function of the Larmor frequency and the slope increases in the intermediate frequencies, finally reaching a region with a different slope at higher frequencies. The plot between relaxation times and frequency (in Hz) at low proton Larmor frequencies, show a longer region having a square-root like behavior, which extends up to intermediate frequencies. This indicates the presence of a longer region with the domination of the DF mechanism at this low frequency range. The NMRD data deviates from this behavior, from about 2 MHz and slightly different slopes were observed at higher frequencies.

3. Thus, the NMRD data in the nematic phase of 40.9 at 75 °C shows at least two different regions with different slopes, and hence a first look at the data suggests that there are at least two possible mechanisms with different frequency dependence.

4. In the conventional NMR region from 6.5 MHz to 45 MHz, temperature dependent $T_i$ data shows an interesting behavior with two different regions in the nematic phase itself.

a). The first region close to the I-N phase transition shows almost a constant $T_i$ with temperature for a range of about 10 °C, particularly at lower frequencies. This trend is different in different frequencies. This temperature independent region close to the I-N phase transition becomes shorter in the case of higher frequencies above 30 MHz.

b). The second region with a stronger temperature dependence closer to the N-SA transition is observed in the nematic phase. This region is longer at higher frequencies. This trend suggests that the SD mechanism becomes more dominant only at high frequencies, around 30 MHz.

5. The SD domination also dominate the smectic A phase near the N-SA transition. There is no sharp change observed at the transition between the N-SA in the collected $T_i$. The strong temperature dependence seen in the nematic phase continues in the smectic A phase also.
6. In the smectic A phase shows similar behavior in all the frequencies from 6.5 to 45 MHz. The continuity between nematic and smectic A phase in the high frequency data suggests that there are common mechanisms which vary continuously with temperature, irrespective of layering. This should be either SD or R, and cannot be DF.

7. The NMRD data collected in the S\textsubscript{A} phase of 40.9 shows (figure 6.40) a different behavior. A strong frequency dependent region is seen below 150 kHz. Another region with a different slope is seen from about 150 kHz to 400 kHz. A third region with a steep variation is seen from around 700 kHz to 20 MHz. Finally, there is a small region that shows a lesser slope from 20 MHz to 45 MHz.

8. A sudden increase towards higher value \( T_i \), at the smectic A to Smectic B phase transition is witnessed, and this occurs within the smectic A phase from at least 2 degrees above this transition. The data in the ordered S\textsubscript{B} phase shows strong temperature dependence and weak frequency dependence in the conventional NMR frequency range. 7) decreases with increasing temperature and decreases with decreasing frequency.

9. The temperature dependent data has shown a weaker pre-transitional effect.

10. The NMRD data collected from 100 kHz to 45 MHz in the S\textsubscript{B} phase exhibits a different behavior, suggesting that the dynamics are very different from that of the nematic and smectic A phases. Three different regions are observed in the NMRD data in the smectic B phase of 40.9. The first region below 400 kHz shows weaker frequency dependence. The second region from 400 kHz to 6.5 MHz, shows a steep variation, and finally reaches a region of lesser slope with frequency dependence.
6.8.2. Data analysis

6.8.2.1 Nematic Phase

6.8.2.1.1. Isotropic elastic constants model

NMRD data analysis was performed assuming isotropic elastic constants ($K_{11} = K_{22} - K_{33} \cdot 1e^6$ dyne) for DF modes. The contributions from various mechanisms to the measured $R_i$ data are shown in the figure 6.38. The dynamic parameters obtained from this fit are summarized in table 6.10. The errors estimated in evaluating the dynamic parameters are around 10 %.

Figure 6.38. Proton relaxation rate ($R_i = 1/T_i$) as a function of frequency in the nematic phase of 40.9 at 75 °C and model fit (eqn 6.1) to three individual contributions to the relaxation rate: director fluctuations (DF), self-diffusion (SD), and molecular reorientations about the short axis (R). Isotropic elastic constants are assumed in evaluating the DF contribution.
<table>
<thead>
<tr>
<th>Model Parameters</th>
<th>Isotropic elastic constants model</th>
<th>Anisotropic elastic constants model</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{11}$ (in $10^{-6}$ dynes)</td>
<td>1</td>
<td>0.516</td>
</tr>
<tr>
<td>$K_{22}$ (in $10^{-6}$ dynes)</td>
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<td>0.344</td>
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<tr>
<td>$K_{33}$ (in $10^{-6}$ dynes)</td>
<td>1</td>
<td>0.745</td>
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<tr>
<td>$A_{DF}$ (in $10^{-6}$ s$^{-2}$)</td>
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<td>1.573</td>
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<td>$q_{sl}$ (in $10^{-1}$/Å)</td>
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</tr>
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<td><strong>0.157</strong></td>
</tr>
<tr>
<td>$\lambda_{sch}$ (in Å)</td>
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<tr>
<td>$\lambda_{isch}$ (in Å)</td>
<td>9.81</td>
<td>11</td>
</tr>
</tbody>
</table>

**Translational self-diffusion (SD)**

| $B$ (in $10^9$ s$^{-2}$) | 3.635 | 1.428 |
| $D$ (in $10^{-10}$ m$^2$ s$^{-1}$) | 3.838 | 0.78 |

**Rotations about the short axis (R)**

| $C$ (in $10^8$ s$^{-2}$) | 0.496 | 0.873 |
| $\tau_R$ (in $10^9$ s) | 75.58 | 67.61 |

The DF contribution is quantified by the constant $A_{DF} = 6.68 \times 10^{-6}$ s$^{-2}$ in the case of the one constant approximation method. In the present case, the upper cut-off frequencies could not be varied and hence they are fixed. The DF contribution needs to be 30 percent of the total relaxation in order to get a reasonable value for upper
cut-off frequency [46]. It should be much more than 100 MHz, assuming molecular
length as the parameter deciding this cut-off. The lower cut-off frequency is about
8.1 kHz, and the corresponding upper cut-off wavelength for the director modes, is
about 3927 Å

Relative contributions

A qualitative picture of the NMRD data fitting in the nematic phase of 40.9 shows that, the DF modes dominate the spin relaxation upto 45 MHz. Rotations about
the short axis show frequency independent behavior from 50 kHz to 400 kHz and
frequency dependent behavior upto 3 MHz. SD becomes more important than R, from
about 2 MHz and becomes comparable to DF, from 30 MHz. Even at high
frequencies, DF is the dominating mechanism over SD. This interpretation is
supported by the weaker temperature dependence observed in the 7% data at
conventional NMR frequencies below 30 MHz. An increasing slope of temperature
dependent $T_1$ data, with increasing frequency suggests that DF domination over SD
decrease with increasing frequency.

A more quantitative picture of the relative contributions can be obtained by
calculating the percentage contributions (at specific frequencies) to the total relaxation.
For example at 50 kHz, the contribution from DF mechanism to the total relaxation is
about 83.5%. The contribution from R and SD are about 12.5% and 4% respectively.
At 400 kHz, the contributions from DF, R and SD are about, 72%, 20.7%, and 7.3%
respectively. Finally R becomes equal to SD at 1.26 MHz. The contributions at
1 MHz are 69% due to DF, 20% due to R and 11% due to SD. At 8 MHz, the
contribution from R becomes negligible. DF and SD contribute 69% and 29%
respectively to the spectral density. At 30 MHz DF contribution becomes 56% and the
remaining 44% relaxation is almost due to the SD mechanism. At the maximum
measured frequency (45 MHz) the contributions from SD and DF are equal.

In the case of rotations about the short molecular axis, the explicit model
parameters used are the amplitude C and the rotational correlation time $\tau_R$, assuming a
simple BPP type contribution [38]. The correlation time obtained for rotations in the nematic phase of 40.9 is $7.558 \times 10^{-8}$ seconds. The contribution to the total relaxation rate from R is quantified by the value $C = 4.96 \times 10^7$ s$^{-1}$. Presence of strong contribution from DF modes in the nematic phase at low frequencies in the kHz region leads to the temperature independent dipolar relaxation times ($T_{ID}$)\cite{11}.

In the case of self-diffusion, the values are obtained for the diffusion constant $D = 3.838 \times 10^{-10}$ m$^2$ s$^{-1}$ are in good agreement with the values obtained from the direct methods in the nematic phases at this temperature range \cite{49}. The frequency independent contribution from SD is extends to frequencies up to about 10 MHz in the nematic phase and a frequency dependent behavior is seen above this frequency.

\textbf{6.8.2.1.2. Anisotropic elastic constants model}

The complete description of the functions and parameters involved in the more generalized model, considering cutoff frequencies as well as anisotropy in the elastic constants have been described in chapter-5. The elastic constants for 40.9 are calculated by extrapolating experimental elastic data \cite{30} obtained in the nematic system 40.4 at different temperatures. The constant ADF obtained for 40.9 is $1.5729 \times 10^{-6}$ s$^{-2}$, which is much smaller than that of the value obtained from the isotropic elastic constants model. The lower cut-off frequency obtained in this case is 156 Hz. The upper cut-off frequencies in the directions parallel and perpendicular to the director are $4.82 \times 10^{8}$ Hz and $10.3 \times 10^{8}$ Hz respectively. The parameters obtained for SD and R contributions are different when comparing with the earlier analysis. It is interesting to note that the anisotropy in the elastic constants influences the relative contributions as well as the dynamic parameters in the case of 40.9. Estimated elastic constants for 40.9 (table 6.10) are much smaller than the values assumed in the case of one constant approximation ($10^{-6}$ dyne) and more anisotropic than the other shorter chain systems in the 40.m series.
Relative contributions

The relative contributions observed from the analysis based on anisotropic elastic constants for DF modes are depicted in figure 6.39. The dynamic parameters are presented in the table 6.10. Typical errors in evaluating these parameters are about 10%. DF mechanism dominates the spin relaxation from 50 kHz to 6.5 MHz, and become equal to SD contribution. From 20 MHz onwards SD become more dominating. At 45 MHz the percentage contributions are 30% and 70% due to DF and SD respectively. The behavior of the NMRD data 400 kHz to 1 MHz is due to the combined effect of SD and DF mechanisms. R and SD contribute to relaxation with a frequency independent behavior below 400 kHz. R contribution becomes negligible from 4 MHz onwards.

Figure. 6.39. Proton relaxation rate \( R_t = I/T \) as a function of frequency in the nematic phase of 40.9 at 75 °C and model fit (eqn. 6.1) to three individual contributions to the relaxation rate: director fluctuations (DF), self-diffusion (SD), and molecular reorientations about the short axis (R). Anisotropic elastic constants are considered for the evaluation of DF contribution.
The correlation time obtained for rotations about the short molecular axis in the nematic phase of 40.9 in this model is $6.76 \times 10^8$ seconds. The contribution to the total relaxation rate from $R$ is quantified by the value $C = 8.73 \times 10^7 \text{ s}^{-1}$. While the correlation time for rotations show a slight variation, the contribution to the total relaxation increases considerably at the cost of the DF contribution in this model.

In the case of self-diffusion, the values $B$ and $D$ are obtained as $1.427 \times 10^9 \text{ s}^2$ and $0.802 \times 10^{10} \text{ m}^2 \text{ s}^{-1}$, respectively. The frequency independent contribution from SD is restricted to lower frequencies upto 8 MHz in the nematic phase. The behavior of the SD contribution is very different from the earlier analysis. SD shows its frequency behavior at much lower frequencies and hence the NMRD behavior of the nematic phase of 40.9 is characteristic to the SD behavior. The stronger temperature dependence seen in the $T_1$ at high frequencies is caused by the presence of this SD. The higher frequency region from 10 to 45 MHz is mediated by SD assisted by DF.

6.8.2.1.3. Comparison with high frequency study

A comparison of the present NMRD study of the nematic phase of 40.9 with the earlier 7) data analysis using a limited frequency range demonstrates the merits and demerits of both the studies. The frequency dependent data from 6.5 MHz to 40 MHz was fitted [1] to various models. It was observed that the analysis of the frequency dependence data of such a small region could not give a completely acceptable picture, though it predicted the domination of the DF contribution in the conventional NMR frequencies. But, the suggested linear behavior of DF contribution with frequency is controversial. The second mechanism predicted by the earlier work (rotations) for high frequency dispersion is different from the present result (self-diffusion). The temperature dependent high frequency data could be best explained by SD+DF contributions rather than DF+R contribution as proposed by the previous study [1]. The high frequency data (6.5 MHz to 45 MHz) was fitted [1] very well to the following models.
Model - 1: \( A \omega^{1/2} + B \) (assuming DF with a square root frequency dependence and rotations with frequency independent behavior) model is the first one fitted the frequency dependent \( T \), data. Fitting was very good in all temperatures [2]. But the constants obtained were unphysical and hence, this model fitting was not acceptable.

Model -2: In the second model, in addition to the DF and R contributions, SD contribution was added in the first model [2]. This was also fitted very well but the diffusion constants and the other model parameters obtained were unphysical. This model therefore, was not accepted.

Model - 3: A replacement of the square-root dependence with the linear dependence in the DF term in the second model given above, also lead to good fitting, but the temperature dependence and the coefficients obtained were found to be unphysical.

Model - 4: Finally, the first model with linear frequency dependence in the DF term fitted well and no temperature dependence was observed. This fitting was considered meaningful. The activation energy associated with the R mechanism was found to be less. The temperature dependence seen in the constant \( A_{DF} \), was attributed to the diffusion assisted DF.

In contrast to the above interpretation, the present NMRD data analysis in the nematic phase of 40.9, using a composite model incorporating DF (anisotropic elastic constants with upper and lower cutoff frequencies), SD and R leads to a better and unique fit, which also gives realistic model parameters. Moreover, the temperature dependence seen in the \( T \), data is also explained reasonably well.

### 6.8.2.2. Smectic A phase

The NMRD data collected in the smectic A phase (figure 6.40) was fitted with the theoretical equation incorporating the three dynamical processes namely 1). Smectic layer undulation modes (LU) (equation 6 3), 2). SD and 3). Rotations about the short axis. The details of the theoretical formalisms for SD and R have been given
in chapter-5. The total spin lattice relaxation rate \( (R_{\text{Tot}}) \) can be written as

\[
R_{\text{Tot}} = R_{\text{LU}} + R_{\text{SD}} + R_{\text{R}}
\]

Figure 6.40. Frequency dependence of the spin-lattice relaxation time \( (T_1) \) in the smectic A phase of 40.9 at temperature 58 °C. Error bars are also shown in figure.

Different contributions to the relaxation data (figure 6.40) in the \( S_A \) phase at 58 °C are shown in figure. 6.41. The parameters for SD and R are given in table 6.11. LU contribution in the smectic A phase is dominates upto 150 kHz in 40.9. R becomes more important from 150 kHz to 2 MHz than LU and SD contributions. SD contributes strongly to the relaxation in the \( S_A \) phase of 40.9 in the conventional NMR frequencies from about 2 MHz and becomes the sole mechanism responsible for spin relaxation. SD contribution is frequency independent upto 2 MHz and frequency dependent from 2 to 45 MHz. The \( T_{\text{ID}} \) data collected earlier [2] in the smectic A phase of 40.9 shows no temperature dependence. This is qualitatively different from the \( T_{\text{ID}} \) data obtained from 40.5 where \( T_{\text{ID}} \) data in \( S_A \) phase is temperature dependent.
Figure 6.41. Proton relaxation rate \((R_i = 1/T_i)\) as a function of frequency in the smectic A phase of 40.5 at 58 °C and model fit to three individual contributions to the relaxation rate: layer undulations (LU), self-diffusion (SD), and molecular reorientations about the short axis (R).

As observed by Schweikert and Noack [47], and Bender et al., [48], it is important to incorporate the R mechanism (about short axis) to explain the intermediate frequency range in the nematic and smectic A phases. Whenever such contribution was not considered NMRD data in the smectic A phase does not seem to fit well [51]. It is also possible to have another R contribution (about long axis) to explain the NMRD behavior at very high frequencies (above 100 MHz).

In the present systems (40, m) R about the short axis seems to be very important in order to explain NMRD data obtained in the nematic and smectic A phases for the present range of frequencies. Rotations about the long axis and segmental motions are also expected to contribute at the high frequencies [12]. It needs to have an almost frequency independent behavior in the measured frequency range (below 50 MHz). But, in the present analysis such a contribution is not
included, since the data fits reasonably well without such contribution. So the present analysis is confined to R about short axis with single correlation time. The parameters obtained for LU contribution are not given in the table 6.11, due to the fact that the dynamic parameters obtained (given manually) are not reliable since the complete dispersion of LU is not observed in the present analysis. The linear behavior of relaxation rate with frequency was given priority rather than the constants and cut-off frequencies. Errors estimated in the evaluation of parameters for SD and R are about 10%.

Table 6.11

<table>
<thead>
<tr>
<th></th>
<th>Translational self-diffusion (SD)</th>
<th>Rotations about the short axis (R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$ ($10^8 \text{ s}^{-2}$)</td>
<td>1.753</td>
<td></td>
</tr>
<tr>
<td>$D$ ($10^{-12} \text{ m}^2 \text{ s}^{-1}$)</td>
<td>1.71</td>
<td></td>
</tr>
<tr>
<td>$C$ ($10^9 \text{ s}^{-2}$)</td>
<td></td>
<td>2.408</td>
</tr>
<tr>
<td>$\tau_R$ ($10^{-9} \text{ s}$)</td>
<td></td>
<td>1.1372</td>
</tr>
</tbody>
</table>

6.8.2.3. Ordered smectic phase (SB)

NMRD data collected in the SB phase of 40.9 was fitted to SD and R mechanisms. The data is shown in figure 6.42. The data fitting is shown in figure 6.43. The dynamic parameters are given in table 6.12. Typical errors in the values of the parameters related to SD and R are about 15% in the case of $S_B$ phase. The low frequency region is completely dominated by the SD mechanism and the high frequency relaxation is dominated by rotations about the long axis. This interpretation is consistent with the observations made with the temperature dependent data (figure 6.37). The observed increase in $T_1$ and $T_{1D}$, near the transition from smectic A to smectic B, in the conventional NMR frequencies clearly demonstrates the difference between the dynamic properties of highly ordered smectic phases and the fluid like nematic and smectic A phases.
Figure 6.42. Frequency dependence of the spin-lattice relaxation time \( (T_1) \) in the smectic B phase of 4O.9 at temperature 40 °C. Error bars are also shown.

Figure 6.43. Proton relaxation rate \( (R_t = 1/T_1) \) as a function of frequency in the smectic B phase of 4O.9 at 40 °C and model fit to the individual contributions to the relaxation rate: self-diffusion (SD), and molecular reorientations (R).
Table 6.12

<table>
<thead>
<tr>
<th>Model Parameters</th>
<th>From $40.9$-$S_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$ (in $10^8$ s$^2$)</td>
<td>1.615</td>
</tr>
<tr>
<td>$D$ (in $10^{-14}$ m$^2$s$^{-1}$)</td>
<td>5.241</td>
</tr>
<tr>
<td>$C$ (in $10^9$ s$^{-1}$)</td>
<td>4.659</td>
</tr>
<tr>
<td>$\tau_R$ (in $10^{-10}$ s)</td>
<td>6.055</td>
</tr>
</tbody>
</table>

Slowing down of the diffusion process and the absence of DF/LU mechanisms are responsible for the sudden increase of $T_1$ in the smectic B near the $S_A$-$S_B$ transition, in the conventional NMR frequencies. In the smectic B phase of the 40.9 the $T_1$ data shows strong temperature dependence. In 40.9, anisotropic rotational diffusion motions of the end hydrocarbon chains, of the entire molecule, or of just the core rigid portions are probable at these temperatures. From the behavior of the data in the SB phase, at the measured temperature ranges, one can conclude that the major contribution comes from rotations of the molecule around the long axis and from the segmental motions. Contributions from the rotations of the CH$_3$ rotations are negligible.

Since there are two alkyl end chains and many CH$_2$ groups present in the system, several rotational diffusion modes could be present, leading to as many values of the correlation time. The $T_{1D}$ data measured in the $S_B$ shows temperature dependence. Reduction of $T_{1D}$ in the $S_B$ phase suggests that, the SD mechanism becomes more efficient since SD sufficiently slows down and influences the dipolar relaxation more efficiently at low frequencies.

In the highly ordered smectic B phase, the diffusion constant becomes very small ($D = 5.24\times10^{-9}$ cm$^2$/s). The relaxation dispersion at low frequencies is explained by the SD process, where one can see a relatively small but frequency independent contribution from R. The temperature dependence seen in the high frequency $T_1$ data with small frequency dependence is consistent with this view. The explanation given for the $T_{1D}$ data, for the $S_B$ phase is also consistent with the NMRD analysis.
R contribution is responsible for the frequency dependence in the $S_B$ phase at conventional NMR frequencies from 10 MHz to 45 MHz. The correlation time associated with the rotation about the long axis obtained from this analysis is $6.06 \times 10^{-10}$ s, which is reasonable when compared to correlation times obtained from NMR studies by Heinze and Grande [24] on nO.m systems. The value obtained by them for rotations about the long axis at temperature $-18^\circ$C in the smectic B phase of 70.4 is $3 \times 10^{-9}$ s. The value obtained for 40.9 is about an order of magnitude smaller than the value obtained by Heinze and Grande [24]. This difference is probably due to the difference in the temperatures of observation.

The activation energy associated with the $T_1$ data in $S_B$ phase is found to be $5.6 \pm 0.5$ kCal/mole [1]. This is in good agreement with the value obtained for the rotations about the long axis in the smectic B phase of 70.4. Heinze and Grande [24] had obtained the value of the activation energy for this dynamics in the system 70.4 as 6.5 kCal/mole. It is therefore, reasonable to say that the rotational contribution obtained in the smectic B phase of 40.9 is mainly due to the rotations about the long axis. The segmental motions are expected to contribute at lower temperatures. The segmental motions observed at lower temperatures in 40.9 with a correlation time of the order of $2 \times 10^{-12}$ s and the associated activation energy for the segmental motions are obtained as 2.8 kCal/mole [1].

Hence, it is concluded that the contribution for relaxation in the $S_B$ phase is predominantly due to the R about the long axis. There should be a weaker contribution from the segmental motions. The experimental correlation times associated with CH$_3$ three-fold rotation in the nO.m series obtained from earlier studies [24] are range from $2.3 \times 10^{-13}$ s (with activation energy 2.75 kCal/mole in 70.4) to $13 \times 10^{-13}$ s (with activation energy 2.1 kcal/mole in 70.4). Comparing the present results with the literature values for CH$_3$ rotations one can say that there is no major contribution that could come from CH$_3$ three fold rotations.
Section 6.9 - Conclusions

**End chain Structure and Molecular Dynamics in 4O.m homologous series of Liquid Crystals**

The results obtained from the NMRD studies of the 4O.m series were discussed in detail considering the systems individually in the preceding sections (sections 6.2 to 6.8). These studies could explain the dynamic behavior of mesophases in each system. It was demonstrated that the individual contributions in mediating spin-lattice relaxation time at different frequencies could be separated out by measuring NMRD at fixed temperature. It was also shown that temperature dependent studies were very useful in obtaining clues about the type of dynamics dominating spin relaxation. In this section, an attempt is made to correlate the dynamic parameters obtained from the NMRD studies of 4O.m systems to the structural parameters which generally influence molecular properties.

**6.9.1. Effect of end chain length on T$_1$**

![Figure 6.44. Spin-lattice relaxation time (T$_1$) as a function of chain length, in the homologous series, 4O.m. The data is obtained at a fixed temperature (T$\approx$65 C).](image)
The figure 6.44. shows an interesting variation of $T_\lambda$ with chain length at a fixed nematic temperature (65 °C) and at different frequencies. Since, the nematic temperature ranges vary with chain length, it is difficult to obtain $T_I$ data at a fixed temperature. In the present case, the $T_I$ values are estimated through extrapolation by simply following the temperature dependence of $T_I$ at different frequencies and systems.

It can be observed from figure 6.44 that the $T_I$ values at low and intermediate frequencies below 20 MHz depends on the chain length. The $T_I$ value increases initially from 40.2 to 40.5 and decreases to low values at longer chain lengths. The absence of such reduction at higher frequencies above 20 MHz suggests that the dynamics observed at high frequencies does not show any systematic variation on the chain length. In other words, there is a strong contribution due to some slow dynamic process, which increases with chain length. This particular dynamics (identified as DF, in the present case) seems to be effective with an increase in chain length. But, it is important to note that there are other properties (odd-even alteration and symmetric end chains) which probably complicate the effect of the chain length. It can be seen in the above figure (6.44) that for the system with $m = 2$ lower $7)$ value is observed, which increase until $m = 5$ is reached, and then decrease upto $m = 9$. It also possible to say that the systems having symmetric end chains (40.3, 40.4 and 40.5) behaves differently. This is probably due to the weaker DF contribution and a stronger contribution from rotations about the short axis and self-diffusion from the symmetric systems. This behavior leads to a sharp increase in $T_I$ in the symmetric systems. This can be justified by the fact that the DF mechanism involves more number of molecules and hence the strong presence of such dynamics would effectively mediate spin relaxation than any other dynamics involving individual molecules, such as $R$ and SD. Hence, a weaker DF mechanism increases the $T_I$ values.

A comparison between earlier results on PAA series [49] and the present $40.m$ series would be interesting. In the PAA series shorter chain molecules (PAA) show higher values of $T_I$, than longer molecules (PAB, HAB) at any particular nematic temperature. In the $40.m$ series, high $T_I$ values are observed when the end chains are close to balanced. At the same time, the $T_I$ values decrease with increasing
chain length when the end chains are imbalanced. The PAA series deals with balanced systems and by increasing the $n$ value, the length of the chains increases at both the ends simultaneously. In the case of the $4O.m$ series, alkoxy chain length is fixed and the alkyl chain length increases. The effect of chain length alone is seen in the PAA series, whereas in the $4O.m$ series, the effect of symmetry complicates the effect of chain length. Even in the case of $4O.m$ series it is observed that $T_1$ decreases with an increase in chain length.

6.9.2. Director fluctuations and end chains

The mode spectrum of DF modes depends on many factors, which include viscoelastic properties of the medium, molecular length, domain size, temperature, and degrees of ordering in the sample [12]. It is important to compare the values of $A_{DF}$, which are sensitive to the viscoelastic constants of the medium. In the present work, the value of $A_{DF}$ is calculated in two different ways (using the isotropic and anisotropic elastic constants models). The $A_{DF}$ values obtained from the NMRD analysis (one constant model for DF contribution) are presented in figure 6.45.

![Figure 6.45. Effect of end chain symmetry on the values of $A_{DF}$](image)

The $A_{DF}$ values are calculated using the isotropic elastic constants model.
Odd-even effects are observed in the values of $A_{DF}$. The values of $A_{DF}$ decreases first with the chain length and then increases with chain length drastically, when the length of the chain is long. $A_{DF}$ value is minimum when $m = 4$. When the number of carbon atoms in the alkyl and alkoxy end chains are equal or close to equal, the value of $A_{DF}$ decreases. The decrease of $A_{DF}$ in the intermediate chain lengths also coincides with the increase of $T$ values for systems having similar chain lengths.

Refractive index anisotropy measured [7] in this 4O.m series is useful in understanding the present results. The maximum value of anisotropy in the refractive index indicates the highest degree of ordering (since refractive index anisotropy is directly proportional to the nematic order parameter S). The higher value of anisotropy observed in system 40.4 could be due to the weaker DF contribution.

From the values observed for $A_{DF}$ and from the arguments given above, it is possible to conclude that the systems with a higher nematic stability and higher value of order parameters show a weaker DF contribution. In the present 4O.m family, higher stability coincides with the symmetry of the end chains. The balanced end chains leading to better stability, probably results from the fact that they show weaker collective director fluctuations.

The $A_{DF}$ values obtained from the anisotropic elastic constants model show a different behavior with the alkyl chain length. $A_{DF}$ decreases with increasing alkyl chain length. $A_{DF}$ values show odd-even effects, which are more pronounced in the case of the anisotropic elastic constants model. Effects of length and symmetry of end chains seem to complicate each other, as well as the odd-even effects in the $A_{DF}$ values. Earlier experimental observations [12] in a homologous series (nOCB) are in agreement with these results. $A_{DF}$ appears to decrease slightly with increasing chain length in the nOCB series. NMRD studies in the PAA series had concluded that the longer molecules have a higher value of $A_{DF}$, which is contrary to the results obtained from the nOCB series.
Figure 6.46. Effect of end chain length on the values of $A_{DF}$. The values of $A_{DF}$ are calculated by the anisotropic elastic constants model. Experimental elastic constants are given as input parameters in the model fit.

Comparing the behavior of $ADF$ values obtained from the isotropic and anisotropic elastic constants models it is possible to conclude that, the value of $A_{DF}$ is very sensitive to the values of the elastic constants ($K_{11}, K_{22}$, and $K_{33}$). Incorporation of experimentally observed (and extrapolated) elastic constants in the model fitting assigns different meaning to the $ADF$ values, and a comparison of $A_{DF}$ values would be meaningful only if the one constant approximation method is adopted. It is clear from these studies that the value of $ADF$ is critically dependent on the choice of model used and the anisotropy of the elastic constants.

Although $ADF$ behaviors are different as observed from these models, the relative contributions from DF modes to the total relaxation are not very different. Comparison of relative contributions from different dynamics to the total relaxation is more important and useful. The percentage contributions of SD, R and DF would be discussed in the sub-section 6.9.5
6.9.3. Self-Diffusion and end chain length

Diffusion constants are known to vary strongly with temperature. In the present case the nematic temperatures, at which the NMRD data was collected are not very different. This gives an opportunity to discuss the importance of end chain structure and properties, in the alteration of the diffusion process. The diffusion constants (D) obtained from NMRD studies are generally not as accurate as the D values obtained from the direct methods.

The D values obtained for 40.4 and 40.5 are of an order of magnitude higher than the values obtained for the other 40.m systems. This anomalous increase of D in the systems 40.4 and 40.5 calls for confirmation, by more direct experiments like the Pulsed Field Gradient NMR method. This increase is probably due to the symmetry of the end chains. Any motion on a molecular level must reflect the shape of the instantaneous potential mean torque on each molecule. Both rotation and translation are expected to be sensitive to the nature of anisotropic interactions, which determine the formation of various liquid crystalline structures [12]. Systems 40.4 and 40.5 not only show high stability, but also very high values of the order parameter when compared to other systems in the 40.m series. The anisotropy in the refractive index measurements made by Potukuchi [7] reveals that the nematic order parameter for 40.4 and 40.5 are much more than the values obtained for the other 40.m systems.

6.9.4. Rotations about the short axis

The qualitative picture of the NMRD analysis shows that the rotations about the short axis are very effective in symmetric systems. DF seems to be more effective in systems having very long end chains as well as in systems having unbalanced end chains (non-symmetric end chains). The correlation times associated with the rotations about the short axis as well as the contribution from this mechanism need to be correlated with the end chain structure. The values obtained from the present NMRD analysis on 40 m systems are tabulated along with the values obtained from the NMRD studies of nematic and smectic systems.
<table>
<thead>
<tr>
<th>System</th>
<th>Mesophases</th>
<th>Correlation time x 10^{-8} seconds</th>
<th>Temperature (in °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6OCB+8OCB</td>
<td>Nematic</td>
<td>0.8</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>Reentrant nematic</td>
<td>2</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>Smectic A</td>
<td>4</td>
<td>37</td>
</tr>
<tr>
<td>1S 1912</td>
<td>Smectic C</td>
<td>9.5</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.5</td>
<td>100</td>
</tr>
<tr>
<td>MBBA</td>
<td>Nematic</td>
<td>24</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.4</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.7</td>
<td>45</td>
</tr>
<tr>
<td>CB7</td>
<td>Nematic</td>
<td>0.25</td>
<td>32</td>
</tr>
<tr>
<td>PCH7</td>
<td>Nematic</td>
<td>0.5</td>
<td>47</td>
</tr>
<tr>
<td>CCH7</td>
<td>Nematic</td>
<td>1</td>
<td>48</td>
</tr>
<tr>
<td>TBBA</td>
<td>Nematic</td>
<td>.05</td>
<td>205</td>
</tr>
<tr>
<td>TBBA</td>
<td>Smectic A</td>
<td>0.1</td>
<td>185</td>
</tr>
<tr>
<td>40.9</td>
<td>Nematic</td>
<td>6.76</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>Smectic A</td>
<td>11.3</td>
<td>58</td>
</tr>
<tr>
<td>40.8</td>
<td>Nematic</td>
<td>3.95</td>
<td>71</td>
</tr>
<tr>
<td>40.7</td>
<td>Nematic</td>
<td>0.373</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Smectic A</td>
<td>4.5</td>
<td>54</td>
</tr>
<tr>
<td>40.5</td>
<td>Nematic</td>
<td>6.4</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Smectic A</td>
<td>4.16</td>
<td>43</td>
</tr>
<tr>
<td>40.4</td>
<td>Nematic</td>
<td>0.58</td>
<td>67</td>
</tr>
<tr>
<td>40.3</td>
<td>Nematic</td>
<td>11.2</td>
<td>69</td>
</tr>
<tr>
<td>40.2</td>
<td>Nematic</td>
<td>2.44</td>
<td>61</td>
</tr>
</tbody>
</table>
The quantitative picture obtained here, as well as in the previous NMRD studies by Noack and coworkers [49] are well supported by the observations made by more simple experiments using dielectric relaxation [41]. The general observation made in the literature [13,32,33,41] says that the correlation times of the order of $10^6$ to $10^8$ s are possible for the rotations about the short molecular axis. In the NMRD studies, rotations about the short axis with correlation times of about $10^7$ to $10^8$ s are easily detectable and the shorter correlation times are generally not observable, probably due to the strong domination of the DF mechanism at the shorter time scales of about $10^6$ s. Dielectric relaxation measurements are sensitive to this time scale, since DF modes do not contribute to the dielectric relaxation [41]. In the present study, slower rotations could be detected probably due to weakening of the DF in the symmetric end chain systems. The constant C, which quantifies the contribution from R, is shown in figure 6.47.

![Figure 6.47](image)

Figure 6.47 A plot between C (represents the contribution from the rotations about the short axis) and the number of carbon atoms in the alkyl end chain. A strong odd-even effect is observed in the value C, which is more pronounced for shorter chain systems.
This figure (6.47) shows that strong odd-even effects are observed in the value of C. Balancing effects are also seen. Both these effects complicate each other. It is interesting to note that the balanced even system 40.4 shows a peak in the value of C. It is known that shorter chain systems show a stronger odd-even effect in almost all macroscopic physical properties. A correlation between the microscopic molecular level dynamic behavior and the macroscopic static physical properties emerge from these studies, though the explanation is not simple as in the case of the microscopic behavior.

In order to understand this complex behavior of the dynamic properties, it is possible to separate odd-even contributions by simply plotting the results of odd and even systems separately. Such a plot is shown in figure 6.48. In order to show the relative variations of all the parameters, and the trends, various parameters are plotted in figure 6.48 in arbitrary units in the logarithmic scale.

Figure 6.48. Different dynamic parameters are plotted (in arbitrary units) as a function of end chain length. Only even systems are considered here. Here, D is diffusion constant, $\tau_R$ the rotational correlation time, B and D are the constants representing the contributions from SD and R. ADF is the contribution from DF.
This figure (6.48) demonstrates the effects of symmetry of the end chains, which overlap with the effects of chain length. In the above figure, only even systems are plotted. Effects of the chain length can be linked with the nature of the end conformer, which is bent in the case of even systems. It can be assumed that the bent conformer interacts more efficiently with the ordering potential rather than the linear conformer, and this may, in principle, affect the rotations and translations in nematic liquid crystals. A closer look at the above figure leads to the following observations and arguments.

1. Strong balancing effects are seen in the dynamic parameters corresponding to the diffusion mechanism.

2. By comparing the values of $\tau_R$ obtained from 40.2 and 40.8, one can say that $\tau_R$ increases with the chain length. In other words, the rotations become slower when the chain length is more. Interaction of the chain with the nematic ordering potential increases with the end chain length, and this leads to a slowing down of rotations. Balancing of the end chains in the case of 40.4 probably decreases the activation energy associated with the rotations about the short axis, and hence more number of molecules involves in the rotations. The increase in the value of $C$ for 40.4 is consistent with this picture.

3. Decrease of the value of $A_{DF}$ in the symmetric system can also be explained on similar lines. Reduction in the activation energy associated with the rotations probably favors this motion instead of DF modes at this time scale. This situation reduces the need and importance of the DF modes at these frequencies. This reduces the overall contribution from DF modes to the relaxation.

The results obtained in the low frequency dielectric relaxation studies [41], on the rotations about the short axis in the homologous series $nS5$ ($n = 5, 6, 7, 8, 9, 10$) are very useful and relevant here. Chrusciel et al., [41] had studied properties such as, dielectric relaxation time, correlation times associated with the rotations, and transition enthalpy, near the I-N phase transition and other transitions (figure 6.49).
Figure 6.49. The clearing temperatures and all dielectric and molecular dynamics parameters obtained for the rotations about the short axis, as a function of chain length in the homologous 4-n-pentylphenyl-4'-n-alkoxythiobenzoate (in short nS5). Here, the symbol || refers to the rotations about the short axis. (after Chrusciel et al [41])

Relaxation times ($\tau$) corresponding to the rotations about the short axis show a low value, leading to an anomalous behavior when the end chains are balanced. Relaxation times are very shorter for systems with $n = 5, 6, 7$ and $8$ when compared with longer chain systems. This means that the rotations about the short axis become efficient when the end chains are close to balanced. It is also observed in these studies that, the activation enthalpy ($AH_\text{a}$) associated with this dynamics also show a
similar behavior. The balanced systems show lower values of activation enthalpy and the longer chain systems, those are unbalanced lead to very high values of activation enthalpies. Though the effect of balancing is not mentioned in the work [41], it is natural to consider this effect, due to the fact that the usual trends expected from chain length and odd-even alternation cannot produce such a change in the trends in the static and dynamic parameters.

The correlation times associated with the rotations about the short axis in the \( nS5 \) series [41] range from \( 2 \times 10^{-8} \) s to \( 10 \times 10^{-8} \) s. Current results obtained for \( 4O.m \) series are comparable with the values obtained from the studies on the \( nS5 \) series (figure 6.49). This comparison of correlation times not only proves the importance of balancing effects but also supports the view that, the rotations observed in the NMRD studies of nematic phases in the \( 4O.m \) series are nothing but the rotations about the short axis. In the case of low frequency dielectric relaxation measurements are direct in nature, whereas in the case of NMRD studies of the \( 4O.m \) series of liquid crystals the R contribution is partially masked by DF at lower frequencies and SD at higher frequencies.

Separation of individual rotations from collective rotational motions (DF) is considered as one of the difficulties faced by experimentalists [50]. Present study reveals that the separation is not very difficult if a proper system and a proper experimental technique like the present one is chosen. In the present work, information about the faster rotations could not be arrived at, mainly because of the non-availability of the NMRD data from 50 MHz to a few hundred MHz. A NMRD study of wider frequency from few kHz to a few hundred MHz can in principle separate out the collective rotations from individual rotations about the short axis, and faster rotations from the slower individual rotations.

### 6.9.5. Relative percentage contributions

So far, different dynamical parameters have been discussed quantitatively based on the model parameters by comparing their absolute values. The discussion
was general in nature, and the relative contributions at different time scales of these dynamics, as a function of the molecular structure have not been compared. The following figures 6.50a to 6.50f, clearly demonstrate the complete picture of dynamic behavior as a function of time window.

The quantitative results as a function of chain length presented earlier, such as D, B, $\tau_R$, C, $A_{DF}$, cut-off frequencies and etc., have strong theoretical basis but they are very complicated. For example, $A_{DF}$ depends on visco-elastic constants of the medium and choice of these constants changes the value of $A_{DF}$. Moreover, explanation based on these parameters necessitates lot more information about the ordering potential and intermolecular interactions.

Though, the values of the dynamic parameters show differences in the analysis, the relative contributions are model independent, except for 40.9. A quantitative analysis of relative contributions as a function of chain length would be more interesting and informative. Relative contributions of DF, SD and R can easily compared if the percentage contribution to the total relaxation can be estimated for different systems at a specific frequency of interest.

Figures 6.50a to 6.50f, show the percentage contributions of director fluctuations (DF), self-diffusion (SD) and rotations about the short axis (R) in the nematic phases of the 40.m systems at spot frequencies, 40 MHz, 30MHz, 20 MHz, 15 MHz, 10 MHz, 5 MHz, 2 MHz, 1MHz, 500 kHz, 200 kHz, 100 kHz and 50 kHz. The frequencies at which the dynamics show significant variation are chosen here. From these figures it is possible to see, how the SD mechanism which is the most dominant one at 40 MHz becomes least important at 50 kHz. Similarly, the DF mechanism, which is a weaker one at 40 MHz in most of the systems, becomes very dominant at 50 kHz. Rotations about the short axis, shows negligible contribution in all the systems at 40 MHz. This remains insignificant at higher frequencies 15 MHz. Importance of R increases from 10 MHz onwards, and R contribution becomes comparable with SD and DF from 2 MHz to 200 kHz. Below 200 kHz DF dominates the relaxation upto the lowest frequency measured.
Figure 6.50a.
DF-SD-RContributions at 40 MHz

Figure 6.50b.
DF-SD-RContributions at 30 MHz
Figure 6.50c.

DF+SD+R Contributions at 20

Figure 6.50d.

DF+SD+R Contributions at 15 MHz
Figure 6.50g.

DF+SD+R Contributions at 2 MHz

Figure 6.50h.

DF+SD+R Contributions at 1 MHz
Figure 6.50i.

DF+SD+R Contributions at 500 kHz

Figure 6.50j.

DF+SD+R Contributions at 200 kHz
Figure 6.50k.

DF+SD+R Contributions at 50kHz

System (m value in 40m series)

Relative contributions (%)

Total

DF

SD

R

Figure 6.501.

DF+SD+R Contributions at 50kHz

System (m value in 40m series)

Relative contributions (%)

Total

DF

SD

R
6.10. References

1. G. Ravindranath, *Ph. D Thesis*, University of Hyderabad, India (1990);


