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Liquid Crystals

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Dielectric studies of liquid crystals: the influence of molecular shape

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INVITED ARTICLE

Dielectric studies of liquid crystals: the influence of molecular shape

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One of the first applications of the molecular field theory developed by Maier and Saupe (Maier W.; Saupe, A. *Z. Naturforsch*. **1958,** *13a*, 564–566) was to the static dielectric properties of a nematic liquid crystal by Maier and Meier (Maier, W.; Meier, G. *Z. Naturforsch*. **1961,** *16a*, 262). Then, in a paper published in 1966 with G. Meier, (Meier, G.; Saupe, A. *Mol. Cryst*. **1966,** *1*, 515) Saupe developed a simple theory to explain the low-frequency dielectric relaxation observed in the nematic phase around 1 MHz, but absent in the isotropic phase, and indeed absent in all other isotropic molecular fluids.

This paper reviews this work of Saupe and the subsequent development of the theory by Martin, Meier and Saupe (Martin, A.J.; Meier, G.; Saupe, A. *Symp. Faraday Soc.* **1971**, *5*, 119), and then by others such as Nordio, Rigatti and Segre (Nordio, P.L.; Rigatti, G.; Segre, U. *Mol. Phys*. **1973,** *25*, 129). These theories described the effect of a nematic potential on the dipole relaxation times for a molecule, and provided a framework within which to analyse experimental measurements of dielectric relaxation in liquid crystals.

The purpose of this review is to examine the application of simple ideas from the theories of Saupe and others to a variety of experimental results for primarily nematic liquid crystals. A particular theme is developed which categorises liquid crystal-forming molecules (mesogens) in terms of their molecular shape. Experimental results of dielectric relaxation for examples of different shaped mesogens are then explained in terms of the theory. Recent work has extended the types of mesogen to include bent-core or V-shaped molecules and flexible-core mesogens, the latter of which, liquid crystal dimers are examples. New features have appeared in the experimental results for these materials, which have stimulated the development of a new theory of dielectric relaxation in flexible dimeric liquid crystals (Stocchero, M.; Ferrarini, A.; Moro, G.J.; Dunmur, D.A.; Luckhurst, G.R. *J. Chem. Phys*. **2004,** *121*, 8079). These results are reviewed.

Keywords: dielectric properties; dielectric relaxation; molecular shape; liquid crystal dimers

1. Introduction

We all have different memories of Alfred Saupe, and a commemorative issue such as this will present a range of facets that together will form an image of our late friend and colleague. But, as in many instances, the whole is so much greater than the sum of the parts. A characteristic that emerges from Saupe's scientific legacy is the enormous range covered by his research interests in liquid crystals. Each of the articles in this volume will refer to particular contributions of Alfred to the body of our knowledge. In this paper, we focus on his work on the dielectric properties of liquid crystals, and show how Saupe's initial studies have been carried forward, and even now point to new developments and understanding in the field.

It is absolutely appropriate that one of the perspectives given of Saupe's work should be on dielectric studies of liquid crystals. In some senses, this is where it all started, through Saupe's connections with the very birth of our subject. He first encountered liquid crystals during his studies for a PhD in physics at the Albert Ludwigs University of Freiburg-im-Breisgau. His supervisor was Wilhelm Maier who had obtained his habilitation degree from the University of Halle in 1943. Maier had studied under Wilhelm Kast (1898–1980) in Halle but, after the liberation of Halle by American forces in 1945, Kast and Maier were relocated to Freiburg. It is through the connection with Kast that Alfred Saupe's work has been anointed by the pioneers of liquid crystals. Kast, although a physicist, had worked alongside Daniel Vorländer in Halle, and what is more, Kast had been supervised by a former assistant of Professor Lehmann, the founding father of our subject. It was Kast who had performed some of the very first experiments on the dielectric properties of liquid crystals in the 1930s [1], and his work had been continued by his former student Maier. So it was not altogether surprising that Alfred Saupe's early encounters with liquid crystals should have involved dielectric studies [2].

The significance of molecular shape in determining the properties of liquid crystals had been recognised from the earliest times [3]. The first liquid crystal-forming

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molecules were quickly identified as rod-shaped (calamitic), and in due course disc-shaped [4] and V-shaped (or banana-shaped) [5] mesogens have taken their place in the hierarchy of structures. To a large extent, the shape of the mesogen determines the types of liquid crystal phases that may be formed. Calamitic phases include nematic and smectic phases, and their chiral analogues, while discotic phases are nematic and columnar. So-called banana mesogens have given rise to a whole new group of B-phases, ranging from B1 to B7. There is, of course, overlap between these phase types, and much work is now focussed on determining the precise structural symmetries of the various phases and to what extent they are related. The molecular shapes mentioned so far are assumed to be rigid, but almost all liquid crystal-forming molecules (mesogens) contain flexible groups. Often these are alkyl or siloxane chains, which help to stabilise fluid phases. However, mesogens have other internal degrees of freedom, such as reorientation about single bonds, rotational isomerisation about carbon–carbon bonds, inversion at a nitrogen atom, and so on. All of these intramolecular structural changes will change the shape of a molecule. So if shape is important to the formation of liquid crystal phases, so also is the range of shapes (conformations) that can be adopted by a mesogen in a mesophase.

Flexibility has long been recognised as an important extra feature to be considered in mesogens. The location of the flexibility in a mesogen is crucial. If it is in attached flexible chains, then the effect of flexibility will be to lower the melting point of the crystal phase, and so allow the appearance of liquid crystal phases. On the other hand if the flexibility is in the mesogenic core, then the effect on properties can be dramatic. Molecules containing such a feature might be termed flexible core mesogens, [6, 7] and be added to the growing list of molecular shapes.

In this paper we will trace the development of some dielectric studies of liquid crystals, starting from the early work of Saupe in the 1960s. The focus will be on how molecular shape influences the dielectric response and, perhaps more usefully, what can be deduced about molecular shape from the analysis of dielectric measurements.

This paper is a tribute to Alfred Saupe, who will always be an iconic and eponymous link to the foundations of liquid crystal science through the Maier–Saupe Molecular Field Theory. However, as will be apparent from all the papers in this Volume, Saupe was always at the forefront of his subject, so it is fitting that the inspiration for this review is also drawn from two very recent papers [8, 9] on bent core liquid crystals, both of which would have been scrutinised with interest by Alfred, had he been alive.

2. Theoretical background

It transpires that the enduring contribution of Saupe to the dielectric properties of liquid crystals is in theory. However, for the theme of this paper, we recall an experimental result from his first paper [10] where he found that the average absorption coefficient (κ) for polarised UV light was the same in the isotropic phase as in the nematic phase $\kappa_{isotropic} = \frac{1}{3}\left(\kappa_{parallel} + 2\kappa_{perpendicular}\right)$ [11]. The correct implication from this observation was that the anisotropy in physical properties in the nematic phase was due to the long-range orientational order of molecules, and not to any special interactions peculiar to the liquid crystal phase. It was this conclusion that prompted the development of the Maier–Saupe theory [12] based on anisotropic dispersion forces between mesogens. Maier and Saupe comment in a subsequent paper [13] that:

> ….. a nematic phase could in principle arise even in the case of spherical molecules, so long as their optical anisotropy were sufficiently strong. This statement appears to be a complete contradiction of the very well-known fact that all substances with liquid crystalline phases are characterised by a strictly elongated shape of their molecules. But in fact there is no discrepancy because the required optical anisotropy can only be found in elongated molecules …

Clearly, Maier and Saupe recognised the importance of molecular shape.

One application of the M–S theory was the formulation of a dielectric theory for anisotropic fluids by Maier and Meier [14]. This theory gave expressions for the electric permittivities parallel, $\varepsilon_{\|}$, and perpendicular, $\varepsilon_{\perp}$, to the director for an aligned uniaxial liquid crystal in terms of the molecular dipole moment and the orientational order parameter, S,

$$\varepsilon_{\|} - n_{\|}^{2} = \varepsilon_{0}^{-1}\frac{NhF^{2}}{3k_{B}T}\left[\mu_{\ell}^{2}(1+2S) + \mu_{t}^{2}(1-S)\right], \quad (1)$$

$$\varepsilon_{\perp} - n_{\perp}^{2} = \varepsilon_{0}^{-1}\frac{NhF^{2}}{3k_{B}T}\left[\mu_{\ell}^{2}(1-S) + \mu_{t}^{2}\left(1+\tfrac{1}{2}S\right)\right], \quad (2)$$

$$\bar{\varepsilon} - n^{2} = \varepsilon_{0}^{-1}\frac{NhF^{2}}{3k_{B}T}\left[\mu_{\ell}^{2} + \mu_{t}^{2}\right]; \quad (3)$$

μ_{ℓ} and μ_{t} are, respectively, the components of the molecular dipole moment along and perpendicular to the molecular long axis, while $n, n_{\|}, n_{\perp}$ are the isotropic (or rms) refractive index, and principal refractive indices parallel and perpendicular to the director.

In these equations an isotropic internal electric field has been assumed, such that

$$h = \frac{3\bar{\varepsilon}}{2\bar{\varepsilon}+1} \text{ and } F = \frac{(2\bar{\varepsilon}+1)\left(\bar{n}^2+2\right)}{3(2\bar{\varepsilon}+\bar{n}^2)}. \tag{4}$$

It is clear from these equations that the average permittivity, $\bar{\varepsilon}$, is independent of S, and should, therefore, vary in a continuous way with decreasing temperature from the isotropic phase to the nematic phase. Molecular shape influences the predicted dielectric behaviour through the orientation of the molecular dipole with respect to the alignment axes of the molecule.

The M–M equations have been extended [15] to deal with biaxial phases consisting of non-axially symmetric molecules, and there have been various attempts to include modifications due to the anisotropic internal electric field [16] and also local dipole–dipole correlations [17]. The latter may change the temperature dependence of the mean permittivity, since dipole–dipole correlations will depend on the order parameter as well as the temperature. Rod-like molecules with axial dipoles tend to arrange themselves in an anti-parallel fashion, giving a reduction in average permittivity, while rod-like molecules with a molecular dipole perpendicular to the rod-axis tend to arrange themselves with the molecular dipoles in a parallel fashion, leading to an enhanced average permittivity [15]. The reverse behaviour is predicted for disc-like molecules [18], but there has been no experimental confirmation of this.

We now turn to Saupe's first contribution to the dielectrics of liquid crystals [2]. This concerned the frequency dependence of the electric permittivity. Both Kast and Ornstein and Meier and Saupe had detected a low-frequency dielectric absorption in the nematic phase of liquid crystals in the region between 0.1 MHz and 4 MHz. This low-frequency absorption is not detected in normal isotropic fluids, and is typically only detected in the parallel component of the electric permittivity in the liquid crystal phase. Meier and Saupe attributed this low-frequency absorption to the reorientation of the fixed part of the molecular dipole about a transverse molecular axis. In a nematic phase, molecular rotation about the transverse axis is hindered by the orientational order. A measure of this was introduced by Meier and Saupe as the retardation factor, g, which is the ratio of the relaxation time for the hindered rotation in the nematic phase, τ_1, to the relaxation time extrapolated from the isotropic phase, τ_0. An expression for g was derived for a two-state model of a dipole flipping in a nematic potential, q, with the result

$$g = \frac{kT}{q}\left(e^{q/kT}-1\right) \tag{5}$$

For reasonable estimates of q, values of g between 100 and 1000 were calculated, which were in reasonable agreement values of g evaluated from measured values of the dielectric relaxation times.

The significance of this result was that it represented the first attempt to solve the rotational diffusion problem in the presence of an orienting nematic potential. Having defined the problem, it was then possible to formulate a more mathematically rigorous solution, which Martin, Meier and Saupe published in 1971 [19]. The basic assumptions of this theory were that the molecule was rigid, and that the permanent dipole attached to the molecule could be resolved into components along, μ_ℓ, and transverse, μ_t, to the molecular axis. Assuming that to first order the orientation of μ_t by an external electric field can occur by rotations about the molecular long axis, then the nematic potential will not affect relaxations associated with the transverse component of the dipole. The 1971 paper [19] just focuses on the behaviour of the longitudinal component of the dipole. Application of a static electric field will produce an induced polarisation, which on removal of the field will relax in the nematic potential. Alternatively, application of a sine-wave electric field of frequency, ω, will result in the induction of a complex polarisation, the real part of which is the dielectric response, and the imaginary part the dielectric absorption or relaxation. For both cases, the relaxation of μ_ℓ could be described in terms of a single relaxation time. Results for relaxation times obtained for application of an external electric field parallel (labelled 1) and perpendicular (labelled 2) to the director were calculated as a function of a nematic potential parameter, q, and are reproduced in Figure (1).

The retardation factors plotted in Figure 1 on the vertical axis are ratios of the relaxation times to the relaxation time, τ_0, for a zero nematic potential, which corresponds to an isotropic state. The parameter q is the height of the potential barrier for reorientation of the molecule about its short axis in the orientationally ordered nematic liquid crystal. For an electric field parallel to the director, the relaxation times (curve 1) for the longitudinal component of the dipole increase rapidly as the strength of the orienting potential increases. If the electric field is perpendicular to the director (curve 2), then according to the theory, the relaxation times decrease with increasing nematic potential strength. Thus, the longitudinal component of the dipole contributes to the perpendicular electric permittivity, but with a relaxation frequency higher than would be expected for the isotropic state. Martin, Meier and Saupe (M–M–S) do not comment on the nature of the dynamics, but remark that it is experimentally difficult to separate this relaxation from the high-frequency relaxation associated with the

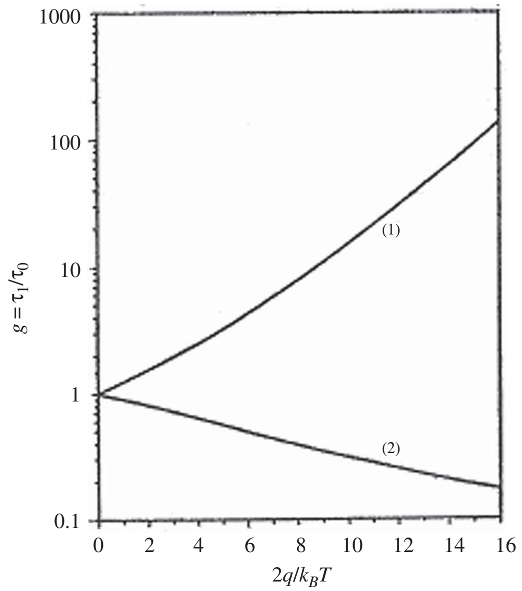

Figure 1. Calculated relaxation times for a dipole in a nematic potential, q, parallel (1) and perpendicular (2) to the director (taken, with permission, from Martin, A.J.; Meier, G.; Saupe, A. *Symp. Faraday Soc.* **1971,** *5*, 119).

transverse component of the molecular dipole. Indeed this would certainly have been the case for the materials available for experimental study at the time.

The work of Saupe and his collaborators was carried forward two years later by Nordio, Rigatti and Segre (N–R–S) [20]. They solved the rotational diffusion equation for the general case of a fixed dipole of arbitrary orientation in a rigid molecule reorienting in an electric field and nematic potential. The method used to solve the problem was similar to that used by Saupe *et al.* [19], but Nordio and co-workers cast the problem and its solution in terms of dipole correlation functions. Their result can be compactly expressed in terms of the time evolution of dipole correlation functions parallel and perpendicular to the director:

$$\left\langle \mu_{\|}(0) \bullet \mu_{\|}(t) \right\rangle = \frac{1}{3}(1+2S)\mu_\ell^2\Phi_{00}(t) + \frac{1}{3}(1-S)\mu_t^2\Phi_{01}(t) \qquad (6)$$

and

$$\left\langle \mu_{\perp}(0) \bullet \mu_{\perp}(t) \right\rangle = \frac{1}{3}(1-S)\mu_\ell^2\Phi_{10}(t) + \frac{1}{6}(2+S)\mu_t^2\Phi_{11}(t) \qquad (7)$$

This result, Equations (6) and (7), may be compared with the result for the static permittivity components obtained by Maier and Meier, Equations (1) and (2). The four terms are directly comparable, relating to the dielectric response of longitudinal and transverse components of the molecular dipole for directions parallel and perpendicular to the director. The M–M equations give the magnitudes of the orientational polarisations, and the N–R–S equations express the dynamics of the corresponding relaxations. Each of the time-dependent angular functions, $\Phi_{ij}(t)$, can be expressed as a sum of exponentials in time or frequency. Numerical calculations by Nordio, Rigatti and Segre showed that each term could be accurately represented by a single first term, which in turn is characterised by a single relaxation time.

The final conclusion of the dielectric relaxation theory initiated by Meier and Saupe was that for a rigid molecule of arbitrary shape in a uniaxial phase there would be four absorptions characterised by four relaxation times, two for the parallel direction and two for the perpendicular direction. These are represented schematically in Figure 2.

The interpretation of these relaxations is as follows. The lowest frequency mode (ω_1) corresponds to an end-over-end motion of the longitudinal component of the molecular dipole. The relaxation (ω_3) corresponds to a precessional motion of the longitudinal component of the molecular dipole, predicted by M–M–S, about the director axis, while the relaxations (ω_2 and ω_4) are at higher frequencies and can be attributed to the motion about the long axis of the molecule. This relaxes components of the transverse dipole moment along and perpendicular to the director. If the local rotational diffusion coefficient is isotropic, then ω_2 and ω_4 are equal.

What does all this tell us about the shape of the mesogen? First, the theory as given above is for rigid molecules, so any changes of dipole moment due to intramolecular rotations are ignored. However, the relative magnitude of the dipole components

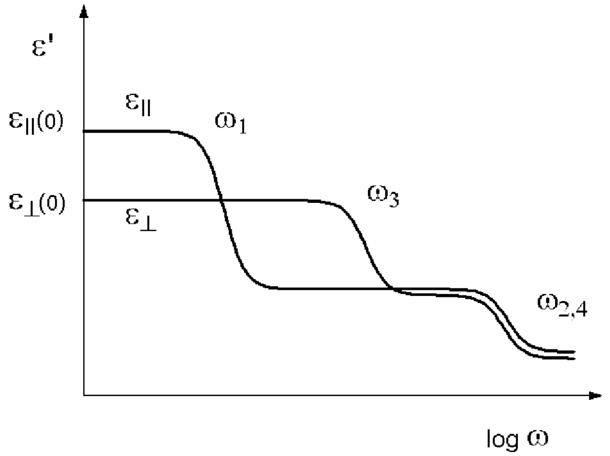

Figure 2. A schematic representation of the variation with frequency of the real part of the permittivity of a uniaxial liquid crystal.

and the frequencies of dielectric relaxations indicate precisely the orientation of the dipole with respect to the alignment axis of the molecule. For rod-like molecules the relative frequencies are as given above; however, for disc-like molecules, it is expected that the dipole component in the plane of the disc (transverse component) will relax at lower frequencies. For V-shaped molecules, the frequencies will be somewhere between those for rods and discs.

3. Experimental results

In principle the theoretical results given previously should apply to any rigid molecule in a uniaxial phase, provided that local intermolecular interactions are ignored, and there is no intramolecular flexibility. Neither of these restrictions apply in practice, and in this section we will review the experimental results available for different molecular species.

3.1 Rod-like molecules

There have been many reviews of the dielectric properties of the liquid crystalline phases of rod-like molecules [21–25]. Results for such systems can be interpreted in terms of the theoretical framework given above. Most authors identify just three relaxations in the nematic phase, which recognises that the frequencies of the two rotations about the long molecular axis ω_2 and ω_4 can be regarded as equal. Of course, the analysis of dielectric spectra in terms of a particular number of relaxations depends on assumptions about the contributing lineshapes. A Lorentzian lineshape is usually associated with a single relaxation process. However, departures from such a line shape can be due to multiple relaxations, or local intermolecular perturbations. Flexibility of the molecules can give rise to broadening of the relaxations, or occasionally to additional dielectric absorption frequencies. These are associated with flexible dipolar groups relaxing independently of the rigid core of the molecule. Such additional relaxations can sometimes contribute to the dielectric spectra of the isotropic phase [26].

In ordered liquid crystal phases such as smectic and columnar phases, dielectric absorption due to collective modes has been detected. Such modes are characteristic of the phase structure rather than the structural features of the constituent molecules, and appear at low frequencies. They are not considered in this review, but have been extensively studied [27].

3.2 Disc-like molecules

Liquid crystalline phases formed from disc-shaped molecules have been of considerable interest in recent years [28]. However, the investigation of their properties is usually much more difficult than is the case for rod-like molecules. The main problem is the difficulty of obtaining well-aligned samples in cells suitable for experimentation. This is particularly true for dielectric studies, and there are no complete results published for disc-like molecules. Those studies that have been reported [29–31] have focussed on particular aspects, and usually only partial results are given.

In the isotropic phase alignment is irrelevant, and results for the dielectric relaxation of disc-like molecules have identified two relaxation modes: a high-frequency mode around 10^9 Hz and a low-frequency mode around 10^6 Hz. This result is not unlike that obtained for some rod-like mesogens, where the high-frequency relaxation is associated with internal reorientation of dipolar groups, and the low-frequency relaxation is a flip-flop motion of the core dipole moment. For disc-like molecules, there are often polar groups attached to the periphery of a rigid core, and these are responsible for the high-frequency mode. This mode persists in lower temperature phases, though being an activated process, the frequency decreases exponentially with decreasing temperature. The low-frequency mode also persists in low-temperature columnar liquid crystal phases, and has been attributed to rotations of the disc-like molecules about the normal to the disc. This requires that there is a net in-plane dipole moment in the disc, either due to the attached polar groups, or to local ordering of the disc-like molecules.

Additional dielectric relaxation modes have been detected in columnar phases for disc-like liquid crystals. In many cases, the low frequency and temperature dependence of these modes indicated that they are collective modes, and so did not reflect any particular molecular motion. For some tilted columnar phases, an additional low-frequency mode could be explained in terms of a relaxation due to the dipole moment perpendicular to the disc [32]. Reorientation of the molecules about the column axis will cause a fluctuating polarisation, which manifests itself as a low-frequency dielectric absorption.

3.3 Bent-core or V-shaped molecules

These represent a class of molecular structures that are between rod-like (calamitic) and disc-like mesogens. As the angle between the arms of a bent-core molecule changes, then their resulting structures embrace those of both rod-like and disc-like mesogens. It should be no surprise then to find that the liquid crystal phases of bent-core molecules include calamitic nematic and smectic phases as well as columnar phases. However, the range of so-called B(anana)-phases also includes new symmetries that are not found for calamitic or disc-like mesogens.

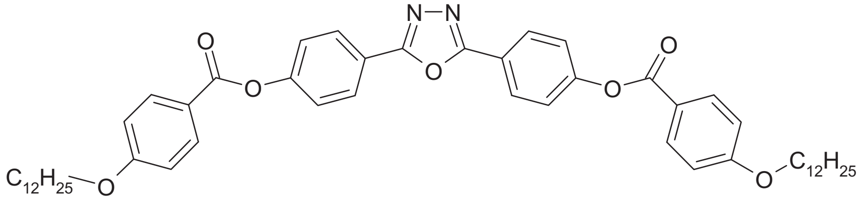

Figure 3. A typical structure (I) for a V-shaped mesogen [33].

The arms of a typical V-shaped molecule (see Figure 3) are usually symmetric, and so there is no dipole moment perpendicular to the C_2 axis. There is, however, almost always a permanent dipole moment along the C_2 axis. Furthermore, although the structures are fairly rigid, there is often the possibility for internal rotations that can modify the structure and contribute to the dielectric relaxation. Due to the bent-structure, whole molecule relaxations about any of the three principal inertial axes will occur at relatively low frequencies. Problems of aligning B-phases have meant that a full dielectric characterisation of these materials is awaited. A number of systems have been studied, and in some cases collective modes identified [34].

Some bent-core mesogens form uniaxial nematic phases, and biaxial nematic phases [35]. For biaxial phases with D_{2h} point group symmetry, the equivalents of the M–M equations have been derived [36]. For measurements along the three principal axes, there are now, in general, three different molecular contributions to the permittivity components from molecular dipole moments labelled as μ_ℓ, μ_t and μ_t'. Each of these may relax at a different frequency, and extending the N–R–S theory to the general biaxial nematic case suggests that there may be up to nine different relaxation times that will characterise the dynamics of the molecular dipole. It is inconceivable that it would be possible to separate these relaxations experimentally, though the theory shows the power of dielectric measurements.

An unusual bent-core mesogen having a double boron bridge has been subject to dielectric relaxation studies [37]. The material, BHC14 (see Figure 4 for the structure) is nematic from 145°C to 117°C, below which temperature an unidentified B-phase appears. Due to the transverse dipole moment, the dielectric anisotropy is negative. In the nematic and isotropic phases, two relaxations have been identified: a dominant mode at around 10^7 Hz, and a higher-frequency mode near 10^9 Hz associated with internal relaxation of the ester group dipoles. For a planar alignment in the nematic phase, measurement of the dielectric response perpendicular to the director gives the perpendicular component of the permittivity, which shows the strong relaxation at 10^7 Hz. This is undoubtedly due to a flip-flop motion of the transverse dipole across the molecular long axis. Application of a bias voltage of 40 V causes the amplitude of this relaxation to decrease substantially. This can be attributed to the induction of a biaxial nematic phase, such that the short axis defined by the plane of the molecule is aligned along the bias-field direction.

A uniaxial nematic phase of a bent-core molecule should exhibit the same features in its dielectric response as any other nematic phase. However, a recent study of such a system [8] has shown that additional relaxations are detected in the dielectric spectrum. The compound studied has a negative dielectric anisotropy. The dielectric response was measured in

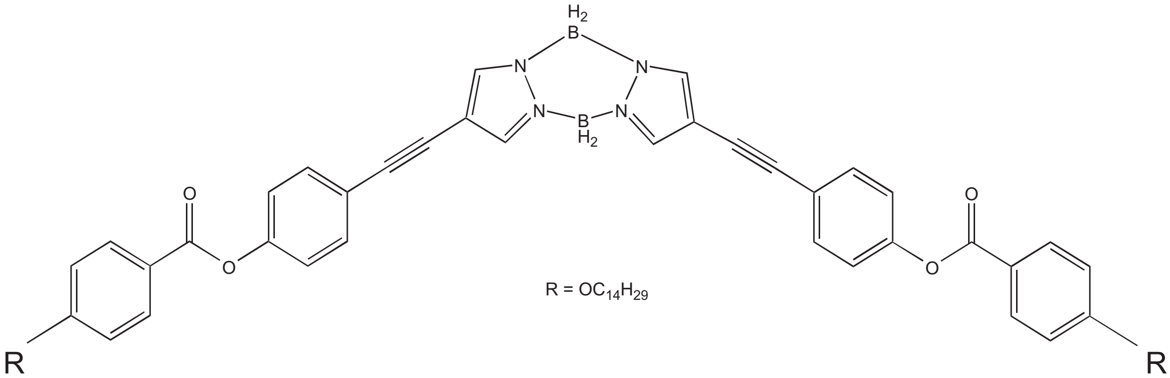

Figure 4. Molecular structure (II) of BCH14 [37].

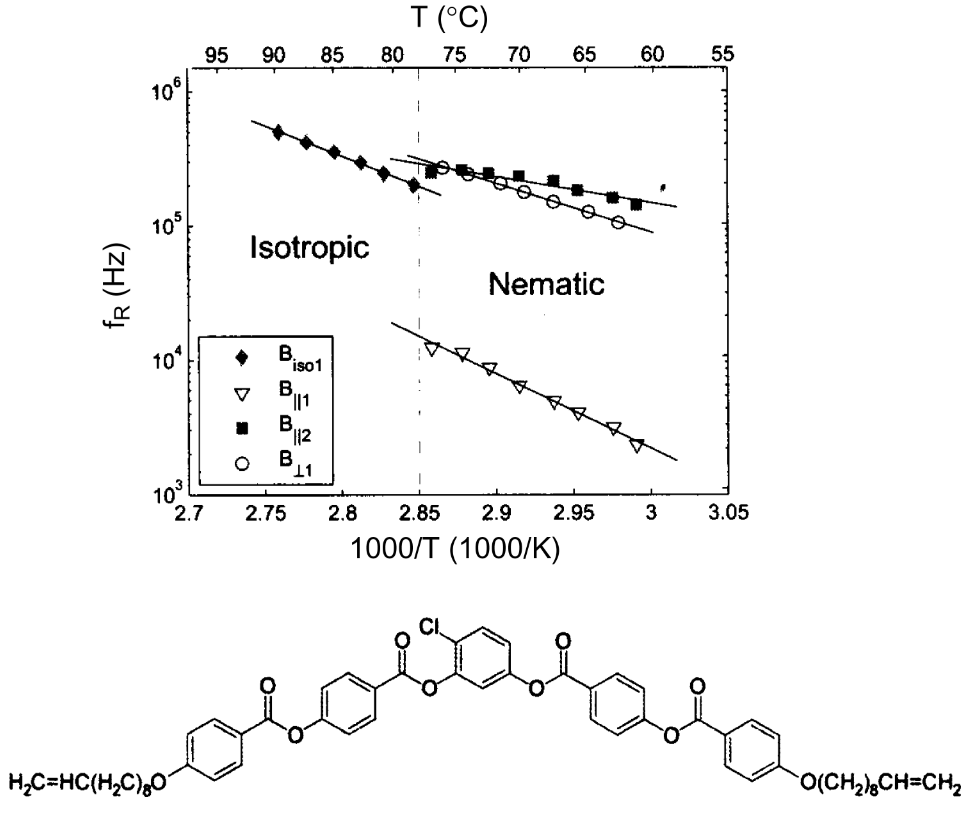

Figure 5. A bent-core molecule (III) which exhibits a nematic phase. The relaxation frequencies labelled B_{iso}, $B_{\|}$ and $B_{\perp}$, refer to relaxations in the isotropic phase and in the nematic phase parallel and perpendicular to the director respectively. (Taken, with permission, from Salamon, P.; Eber, N.; Buka, A.; Gleeson, J.T.; Sprunt, S.; Jakli, A. *e-Liq. Cryst. Comm.* **2009**).

samples aligned by an external magnetic field, and results for the relaxation frequencies detected are plotted as a function of inverse absolute temperature in Figure 5. In addition to the relaxations measured, the authors indicated that for both the isotropic and nematic phases there were additional high-frequency relaxations associated with an internal relaxation of molecular dipoles.

Molecular calculations confirmed that the molecular dipole made an angle of 74° to the molecular axis, greater than the magic angle of 54.7°, which indicated that the liquid crystal would have a negative dielectric anisotropy (measured value $\Delta\varepsilon \sim -1.7$). In order to obtain agreement between the calculated molecular dipole moment and that determined from measurements of the isotropic permittivity, it was necessary to assume that a number of low-energy conformations of the molecule contributed to the average structure at the experimental temperatures. Although the data is not given explicitly in the quoted paper, it can be deduced that the average permittivity in the nematic phase is about the same as that in the isotropic phase. This suggests that the distribution of conformations does not change significantly over the temperature range of measurements, so the average shape of the bent-core molecule remains approximately fixed. Measurements of the dielectric properties of mixtures of the bent-core mesogen with a low molecular weight nematic mesogen of similar chemical constitution, showed an approximately linear dependence on concentration. This result also provides evidence that the average shape of the bent-core mesogen is not changing substantially under the varying experimental conditions. A discussion of the physical processes likely to be responsible for the observed dielectric relaxations is deferred until we have considered the dielectric response of bent-core mesogens having a flexible core.

3.4 Flexible-core molecules

An unusual group of liquid crystal-forming molecules known as dimeric mesogens have been the subject of considerable attention in recent years [38]. These molecules consist of two mesogenic groups connected by a flexible methylene or siloxane chain. Two particular aspects of these molecules are the strong dependence of their liquid crystal properties on the parity of the connecting chain (odd-even effects), and also the variation of mesophase properties with the length of the chain.

Dimeric mesogens have been prepared with identical mesogenic groups attached to the chain (symmetric dimers) and with differing groups attached (non-symmetric dimers). Symmetric dimers with polar terminal groups are of interest dielectrically because the longitudinal component of the dipole moment is zero by symmetry. Furthermore, the average dipole moment measured will depend on the range of conformations adopted by the connecting chain, which will, in part, be determined by the chain length and parity.

Measurements of the static permittivity components of a number of symmetric dimers have been reported [39], and show that the average permittivity has a discontinuity at the nematic to isotropic transition, and decreases strongly with decreasing temperature in the nematic phase. This behaviour is illustrated in Figure 6 which gives the variation of the permittivity components as a function of temperature for a simple symmetric dimer consisting of two cyanobiphenyl groups connected by a C_7 methylene chain [40]. Symmetric dimers having groups with longitudinal dipoles also exhibit a low-frequency relaxation, similar to that observed for dipolar monomeric mesogens, though the strength decreases with decreasing temperature.

The average permittivity depends on the mean-square dipole moment, and the dielectric results indicate a significant structural change at the transition. Furthermore, the strong variation with temperature in the nematic phase is suggestive of a progressive structural change throughout the nematic phase. This structural change also affects the individual components of the permittivity, such that the dielectric anisotropy changes from a relatively large value to almost zero, or even negative at low temperatures. These effects can be modelled theoretically by allowing the dimeric mesogen to adopt different conformations and statistically averaging the dipole components. It is worth pointing out that satisfactory agreement between experimental and calculated results can only be achieved if a full rotational potential about carbon-carbon single bonds is used to model the flexibility of the methylene chain. It seems that the widely used RIS (rotational isomeric state) model is not sufficiently versatile to allow accurate modelling of the dielectric properties of flexible dimeric mesogens [41, 42].

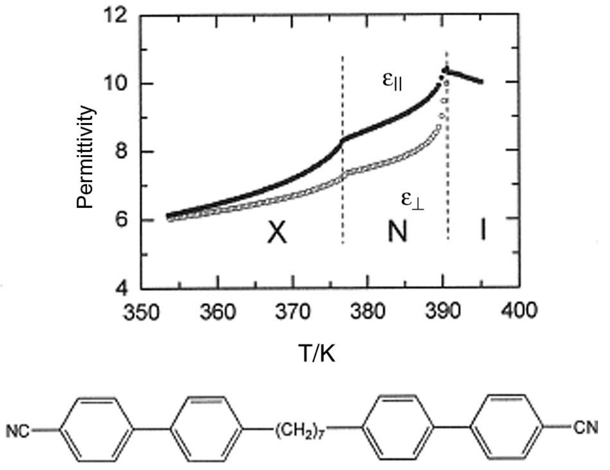

Figure 6. The principal permittivity components of CB7CB (IV) as a function of temperature through the nematic phase and an as yet unidentified low-temperature liquid crystal phase. The unidentified X phase has been extensively studied using a variety of techniques and is possibly a new type of nematic phase or a modulated phase with very low positional order [47].

The conclusion from theoretical modelling of the static dielectric measurements is that the conformational distribution for symmetric dimeric mesogens changes substantially at the isotropic to nematic phase transition, and also changes with temperature in the mesophases. From an almost random coil distribution [43, 44] in the isotropic phase, the chain conformations become increasingly constrained by the long-range orientational order in the nematic and lower temperature liquid crystal phases. Such an effect can have a dramatic influence on the physical properties of dimeric liquid crystals.

A linear molecule of $D_{\infty h}$ symmetry has no longitudinal or transverse dipole moment. Symmetric dimeric mesogens, as normally represented by an extended structure, have no longitudinal component of the dipole moment. Assuming free rotation of the extended molecule, linear conformations of a dimeric mesogen possess a D_{∞} axis, which is the alignment axis in the liquid crystal phase. However, chain flexibility generates lower symmetry bent structures, having C_{2v} symmetry. Molecules of such a structure will have a dipole moment along the C_2 axis. A bend angle for C_{2v} conformations of symmetric dimeric mesogens may be defined as the angle between the axes of the terminal groups. In a linear extended structure the angle between the terminal groups is 180°, i.e. they are antiparallel. Small departures from $D_{\infty h}$ symmetry arising from molecular bend in dimeric mesogens will induce a dipole moment along the C_2 axis, which is perpendicular to the D_{∞} axis. However, for small deviations from a linear structure, it may be assumed that the average alignment axis of the molecule will still be approximately along the D_{∞} axis of the linear conformation. There will, however, be a lateral component to the dipole moment detected in dielectric measurements. As the molecule becomes more bent, the angle between the terminal groups decreases from

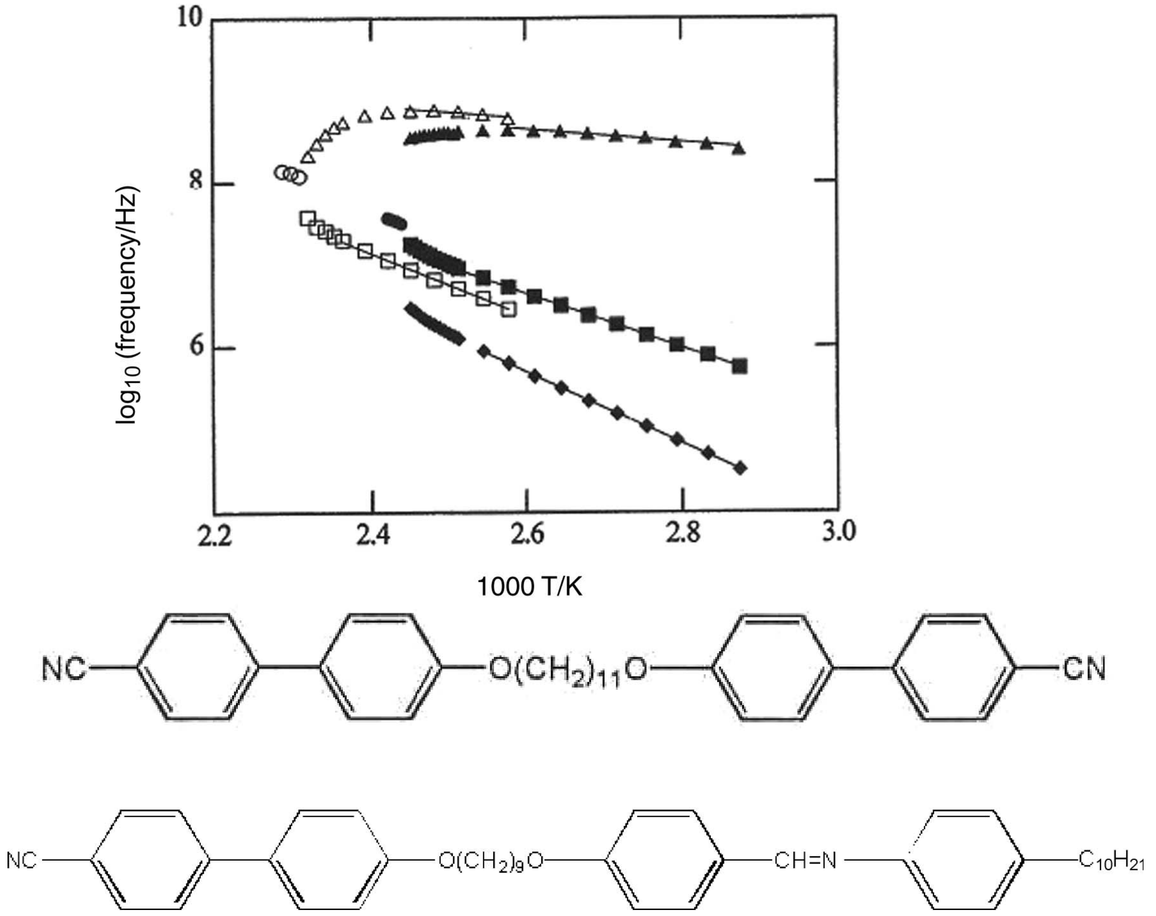

Figure 7. Relaxation frequencies of the symmetric BCBO.11 (V) and non-symmetric CBO9O.10 (VI) plotted on a logarithmic scale as a function of inverse absolute temperature. Symmetric dimer BCBO.11 (V): relaxation frequencies depicted with open symbols: ○: isotropic, △: high-frequency mode, □: low-frequency mode. Non-symmetric dimer CBO9O.10 (VI): relaxation frequencies depicted with closed symbols: ●: isotropic, ▲: high-frequency mode, ■: intermediate-frequency mode, ◆: low-frequency mode.

180°, and the alignment axis of the molecule may change. For an angle of 90° between the terminal groups, the molecule resembles a disc, and the alignment axis then would be perpendicular to the molecular structure, while for molecular conformations having a bend angle less than 54.7°, the alignment axis of the molecule will become the C_2 axis. In reality, the alignment of the director axis in a liquid crystal of a flexible molecule will be determined by an average over all the molecular conformations. Measurements of the dielectric absorption in symmetric dimeric liquid crystals can provide information on the structural changes that occur as a function of temperature.

Frequencies for the dielectric relaxation modes detected in a symmetric dimer BCBO.11, and an asymmetric dimer CBO9.O10 are plotted in Figure 7 on a logarithmic scale as a function of inverse absolute temperature. For the symmetric dimer, there are two relaxations, as expected, for which the activation energies for the high and low-frequency modes are 14 kJ mol^{-1} and 72 kJ mol^{-1}, respectively. The latter can be compared with an activation energy of 52 kJ mol^{-1} for the end-over-end dipole relaxation in a monomeric mesogen of comparable structure, namely 4-heptyl-4′-cyanobiphenyl.

The dielectric properties of non-symmetric dimers having different end groups have also been studied [39, 40]. The distribution of chain conformations will be similar to those for symmetric dimers, but the consequences for the dielectric properties are quite different. For non-symmetric dimers there is always a longitudinal component of the molecular dipole moment, and the variation of the static permittivity components with temperature is similar to that observed for typical monomeric mesogens with a positive dielectric anisotropy. The average permittivity as a function of temperature is almost independent of temperature, suggesting little influence of molecular shape on the measured static dielectric properties.

However, measurements of the dielectric absorption of non-symmetric dimers as a function of frequency do yield information on the changes of shape that occur through changes of conformational distribution in the nematic phase. Two well-separated absorptions are detected at lower frequencies, both having the characteristics of a typical end-over-end relaxation. In addition, a higher frequency relaxation was detected. An Arrhenius plot of the relaxation frequencies is given in Figure 7, where a comparison can be made with results for a typical symmetric dimer.

A non-symmetric polar dimer in a liquid crystal phase has a number of different conformations which contribute to the dielectric response. These represent a range of geometries, for which the corresponding dipole moments will vary, and may be expected to relax at different frequencies. However, our experimental evidence is that the observed absorption curves in the frequency range 10^5 Hz to 10^8 Hz, far from being broadened through fluctuations in local fluid structure, can in fact be well-represented by two separable Lorentzian lineshapes. This prompted the formulation of a theory for the dielectric relaxation of mesogenic dimers in a nematic phase based on a time-scale separation for the motion of the flexible chain and the terminal end groups [41].

We recall that the original model of Meier and Saupe for the dielectric relaxation of a dipolar molecule in a nematic potential was a two-state model representing the two orientations of a dipole along the director axis. The model we have developed for dimeric mesogens, whether symmetric or non-symmetric, is a four-state model for the connected terminal groups, parallel or anti-parallel to the director. This model is represented in Figure 8. The model assumes that the chain dynamics are fast enough not to influence the relaxation of the dipolar end groups. Orientational relaxation of the end groups with respect to the director proceeds via the flip-flop processes indicated in the figure. The relative rates for flipping of the different terminal groups is determined by their rotational diffusion coefficients, and the nematic potential experienced by the terminal groups. Calculations were performed for a number of model systems, including symmetric dimers having identical polar terminal groups, and non-symmetric dimers with the dipole located on one or other of the terminal groups.

For a relaxing system, as in Figure 8, but in which the two terminal groups are identical, and have non-zero longitudinal dipoles, a single relaxation time is predicted with an intensity that diminishes with increasing order or decreasing temperature, as shown in Figure 9.

For a non-symmetric dimer in which the dipole moment is located in the smaller terminal group 1, (see Figure 8), the calculated dielectric dispersion curve is given in Figure 10(a). The parameters of the model are the relative rates of flipping for the two end groups, and the equilibrium proportion of *trans* to *cis* conformers, P_T^{eq}. The latter determines the temperature. Thus at the lowest temperature, it is assumed that

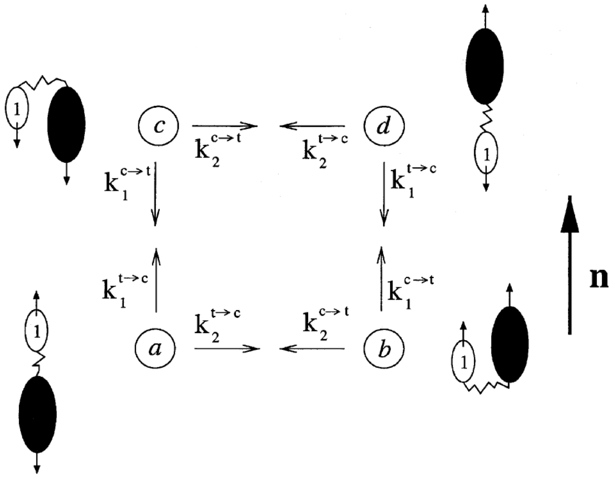

Figure 8. The four-state model for the reorientation of a dimeric mesogen in a nematic potential. The vector **n** denotes the director. The terminal groups can be polar or non-polar, and may be the same size or different. The two allowed conformations for the dimer are designated as *cis*(c) and *trans*(t). Kinetic inter-conversion processes permitted by the model are indicated.

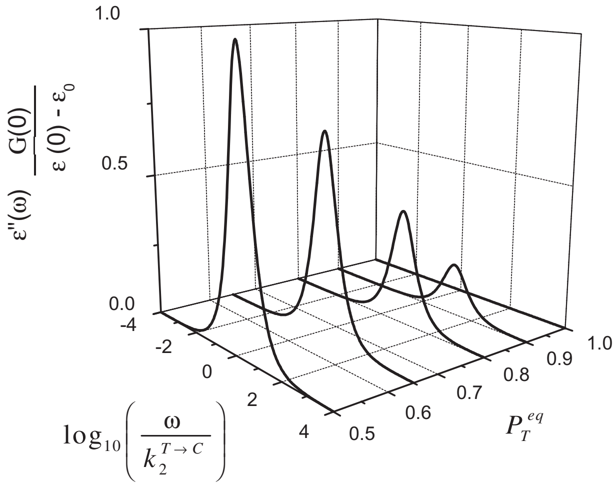

Figure 9. The calculated dielectric absorption (vertical axis in reduced units) of a symmetric dimer as a function of the logarithm of reduced frequency, and as a function of the population of the *trans*-dimers (P_T^{eq}). The latter is equivalent to the order parameter [41] or decreasing temperature.

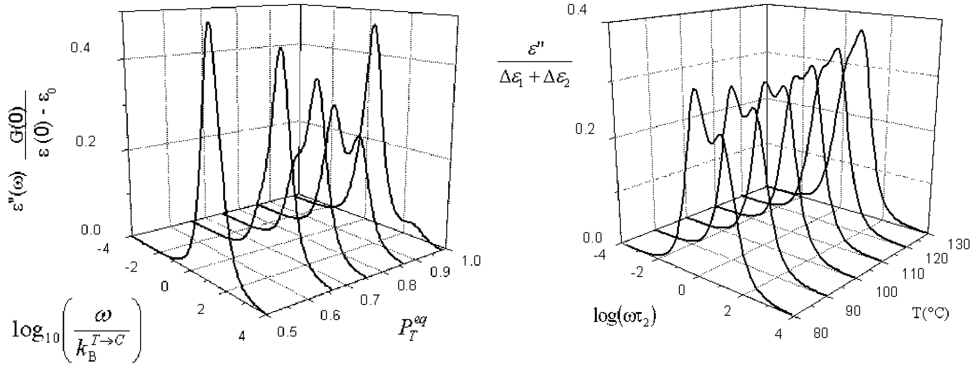

Figure 10. (a) Calculated dielectric absorption [41] for a non-symmetric dimer. (b) Experimental dielectric absorption [41] for the non-symmetric dimer CBO9O.10.

the value of P_T^{eq} is unity, corresponding to an all-*trans* composition. It is seen that over the range of temperature (represented by $P_T^{eq} = 0.5$ to $P_T^{eq} = 1.0$: high to low) the maximum in the dielectric absorption shifts from high frequency to low frequency. This occurs via a bifurcation which can be correlated with two kinetic processes: the low-frequency process involves a flip-flop motion of the larger terminal group, while the higher-frequency process involves a flip-flop of the smaller group.

The theoretical results in Figure 10(a) may be compared with the experimental results obtained for the non-symmetric dimer CBO9O.10. Dielectric absorption measured at low frequencies in the nematic phase as a function of frequency and temperature are shown in Figure 10(b). It is important to note that the temperature scale in Figure 10(b) goes from low temperature to high temperature, whereas the scale of P_T^{eq} in Figure 10(a) corresponds to a change from high to low temperature.

The dimeric mesogen CBO9O.10 (VI) represents a molecule having a longitudinal dipole in the smaller of the two terminal groups. Experimental results in Figure 10(b) show that there are two low-frequency absorptions, with the lower-frequency relaxation dominating at low temperatures. The frequency of maximum absorption shifts to high frequency via a bifurcation, exactly as predicted by the theoretical results given in Figure 10(a).

The similarity between the experimental and calculated results for the simple four-state model is such that the experimental data can be fitted to the model. One result of this fitting is the equilibrium concentration of *trans* conformers in the nematic phase as a function of temperature. Results for P_T^{eq} obtained from this fitting of the data given in Figure 10(b) are presented in Figure 11. Within the assumptions of our model, the results of Figure 11 show that the proportion of *trans* conformers falls from 0.85 to 0.75 over the temperature range of the nematic phase of CBO9O.10. This provides clear evidence from dielectric measurements of a change in the average shape of the mesogen in the liquid crystal phase as the temperature changes.

Dielectric measurements have also been reported [45] for a flexible core mesogen in which the terminal dipolar groups are connected laterally to the linking chain; the latter being a methylene chain with a siloxane central linkage. The compound studied was a dimer formed by reacting 4′-undecyloxy-biphenyl-4-yl 4-octyloxy-2-5-(1,1,3,3,-tetramethyldisiloxanyl)-pent-1-yloxy-benzoate with 4′-(4-octyloxybenzoyloxy)biphenyl-4-yl 4-octyloxy-2-(pent-4-en-1-yloxy)benzoate: its structure is given in Figure 12.

The compound VII is nematic from 109°C to –9°C, where a glass transition was observed, and the dielectric anisotropy of the nematic phase was negative. Results for the measured relaxation frequencies as a

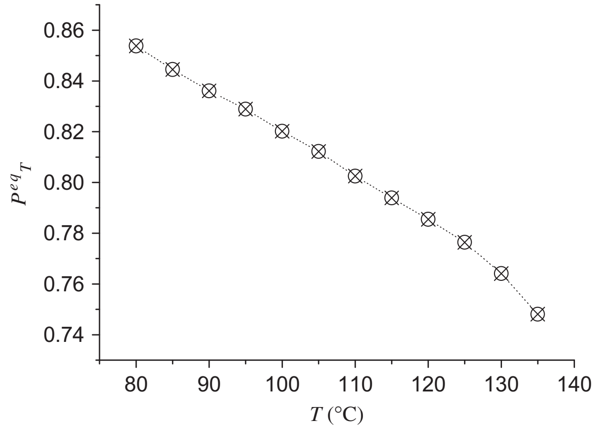

Figure 11. The variation of the proportion of the *trans* conformer of CBO9O.10 as a function of temperature, obtained by fitting experimental measurements to the four-state model.

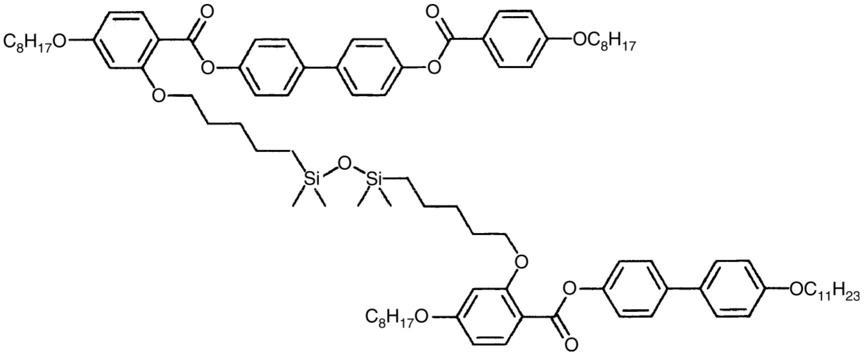

Figure 12. A non-symmetric dimer (VII) linked through alkoxy-chains and a siloxane group.

function of inverse temperature are given in Figure 13. In the isotropic phase there were two relaxations, a high-frequency mode ($\sim 10^9$ Hz) associated with intramolecular relaxations of the polar ester groups of the terminal groups, and the other a low-frequency Debye-type relaxation around 1 MHz, which we attribute to an end-over-end reorientation of the polar terminal groups. The high activation energy ($\sim$80 kJ mol^{-1}) for this process is no doubt related to the extended length of the polar groups.

In the nematic phase, four relaxations were detected. The high-frequency internal mode 1 (▲) persisted throughout the nematic range, though its intensity decreased with decreasing temperature. The lowest frequency mode 4 (□) appeared in the region of 10^5 Hz. The activation energy (84 kJ mol^{-1}) of this mode is similar to that in the isotropic phase, and so we attribute this to Debye-like end-over-end rotation of terminal groups. The other two modes of intermediate frequencies do not exhibit a normal Arrhenius variation with temperature. The activation energy of mode 3 (■) is almost zero just below the nematic to isotropic transition temperature, and increases as the temperature decreases. This mode dominates the dielectric response at low temperatures, and has the characteristics of a collective mode.

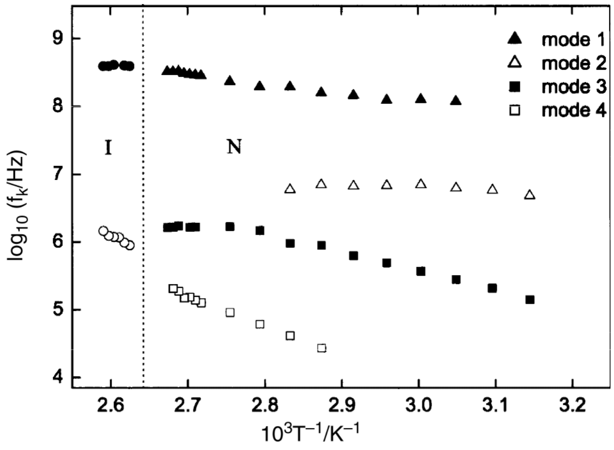

Figure 13. Relaxation frequencies as a function of inverse absolute temperature for compound VII.

4. Discussion

The starting point for this paper was the proposal by Meier and Saupe [2] that measurements of the dielectric relaxation times could be used to probe the orientational order of nematic liquid crystals of rod-like molecules. A molecular dynamics simulation study of the rotational diffusion of Gay-Berne particles has been performed by Luckhurst and Bates [46] to compare with the predictions of Meier and Saupe and the later theory developed by Martin, Meier and Saupe [19]. While results from the theory and simulations are qualitatively similar, in particular predicting a rapid increase in orientational correlation times with increasing order, the theory tends to underestimate the orientational order parameter by up to approximately 0.1. An interesting revelation of the simulation study was the dependence of orientational correlation times on density as well as temperature. The theory of Martin, Meier and Saupe [19] does not include any dependence on free-volume, and this is one of the factors likely to be responsible for the lack of agreement between the theory and simulation results. A suitable new theory has yet to be formulated.

This paper has reviewed the results of a number of studies of dielectric response in nematic liquid crystals. Like Saupe, the focus has been to obtain information about molecular motion from the experimental measurements of electric permittivity. The range of molecules that form liquid crystal phases and indeed the phase types identified continue to expand. Molecules are never as simple as our depictions of them, and it is not surprising that the interpretation of experimental results is challenging. While molecular shape is a useful concept for categorising liquid crystal behaviour, it has to be recognised that for many liquid-crystal forming molecules the shape is a fluctuating variable. It seems that the dielectric response is particularly susceptible to molecular shape, partly because changes of shape are often accompanied by changes of molecular dipole, but also because dielectric properties probe the environment of relaxing dipoles, which is shape-dependent as well.

Despite the complexity of dielectric theories, it seems clear that there are modes characteristic of molecular reorientation in liquid crystals. There are also collective modes, mostly in smectic and columnar phases, but these can usually be identified by their lineshape and the non-Arrhenius variation of relaxation times with temperature.

To return to one of the papers that introduced this review: recent work [8], in part from Saupe's former research group, reported the dielectric properties of a bent-core liquid crystal. High-frequency relaxations associated with reorientations about the long molecular axis were beyond the range of the measurements. However, the relaxations identified in the frequency range reported are not inconsistent with the results we have reported here for a number of mesogens of different molecular shapes. The lowest frequency relaxation is usually Debye-like and represents an end-over-end reorientation of an effective molecular dipole. This can be strongly retarded by the ordered environment as indicated by large activation energies. Relaxations at intermediate frequencies are usually associated with precessional motion, which may couple with the local environment to develop collective modes.

Recent work by Goodby and others [9] on compounds similar to I (see Figure 3) have revealed unusual properties in their nematic phases. The compounds reported were substituted bis-(phenyl)oxadiazoles having alkyl chains attached to one of the arms of the V-shaped core. This substitution destroys the C_{2v} symmetry of the molecule. The resulting materials exhibit nematic phases and lower temperature phases of as yet unknown identity. Features of the optical textures, calorimetric and X-ray measurements led the authors to speculate that kinetically driven molecular structure changes may be responsible for the observed effects. Changes in shape at the molecular level are apparently determining the macroscopic liquid crystalline phase behaviour.

The key result from the paper of Meier and Saupe [2] was that the long-range order in a liquid crystal changed the molecular dynamics, and this was measurable using dielectric relaxation measurements. In this review we have shown that dielectric measurements can now reveal changes of molecular structure, and indeed give clear indications of dynamic changes in structure induced by long-range molecular ordering in liquid crystalline phases.

Group Photo. A group from the 1993 Gordon Conference on liquid crystals, Wolfeboro, New Hampshire sets off for a summit in the White Mountains. In the foreground from left to right, Neville Boden, Alfred Saupe, David Dunmur, Wojciech Otowski and Günter Scherowsky.

Alfred Saupe went on to initiate many other investigations of liquid crystals using a variety of techniques. He did not seek fame and recognition, but his work will live on as long as liquid crystals are studied. He was most at home in the laboratory, guiding experiments, encouraging students and co-workers, and providing acute advice. Science was an important part of Alfred's life, but not the only part. He was devoted to family and never lost his fondness for the mountains of his youth. Whether in the lab, on the ski slopes, or on a mountain hike, Alfred Saupe was a delightful companion, and a good friend and colleague to many.

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