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H. F. Gleeson[a]; C. D. Southern[a]; P. D. Brimicombe[a]; J. W. Goodby[b]; V. Görtz[b]
[a] School of Physics and Astronomy, University of Manchester, Manchester, UK [b] Department of Chemistry, University of York, Heslington, York, UK

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INVITED ARTICLE

Optical measurements of orientational order in uniaxial and biaxial nematic liquid crystals

H.F. Gleeson[a]*, C.D. Southern[a], P.D. Brimicombe[a], J.W. Goodby[b] and V. Görtz[b]

[a]*School of Physics and Astronomy, University of Manchester, Manchester, UK;* [b]*Department of Chemistry, University of York, Heslington, York, UK*

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The use of optical methods to study the orientational order in nematic liquid crystals is both convenient and powerful. Some of the earliest approaches made use of measurements of the refractive index anisotropy, following the methodology of Halle [1] to measure the order parameter, $\langle P_2 \rangle$. This method is reviewed briefly and some typical areas of application are presented. Raman spectroscopy is a second approach discussed in this paper. Although technically a more complex methodology, Raman spectroscopy has the significant advantage that in addition to being able to measure $\langle P_2 \rangle$ it is also possible to determine $\langle P_4 \rangle$. A review of current approaches is presented. Very recently, it has been shown that polarised Raman spectroscopy can be employed to determine biaxial order parameters in liquid crystals. The methodology is described, and data are presented for such measurements on a series of bent-core nematic materials that could exhibit the elusive biaxial nematic phase.

Keywords: orientational order parameters; polarised Raman spectroscopy; biaxial order

1. Introduction

The dynamic orientational ordering of the constituent molecules within liquid crystal phases, particularly the nematic phase, is the defining property of a liquid crystal, and has thus been the subject of extensive study. One of the most popular approaches to the measurement of orientational order in liquid crystals has been to examine the optical properties of the system, and this paper reviews two of the key methods that have been adopted to determine the order in nematic liquid crystals using optical techniques. The first methodology considered relies on the determination of the birefringence of a material, and has the merit of being based on a simple measurement using apparatus available in many laboratories. However, this approach can determine only the simplest information relating to order and the apparatus used may often have significant restrictions, making it unsuitable for materials which exhibit liquid crystallinity at high temperatures, or which are difficult to align. The second method described in this review paper is based on polarised Raman scattering, which in principle allows much greater detail of the order in a liquid crystal system to be determined. However, this approach requires rather more expensive apparatus, in addition to detailed computer fitting of the results, in order to obtain the order parameters from the data. This paper describes the basis of the two approaches and provides results giving examples of each technique.

Central to the studies of order in liquid crystals is the statistical analysis which allows the orientational order of the system to be quantified. The widely accepted Maier–Saupe (MS) theory [1] successfully predicts many of the features of the nematic phase that are observed experimentally, including the first-order transition between the disordered and ordered states. The orientational order parameter, S, is defined in

$$S = \frac{1}{2}\left\langle 3\cos^2\beta - 1 \right\rangle, \tag{1}$$

where the angular brackets indicate a statistical average and β is the Euler angle, which describes the orientation of the molecular symmetry axis with respect to the director. The Euler angles used in this paper are defined in Figure 1.

Following the work of Maier, Saupe and others [2, 3], Humphries *et al.* developed a pseudo-potential for rod-like molecules [4] and deduced self-consistency equations which allowed the temperature dependence of the order parameters associated with the first two Legendre polynomials to be determined:

$$P_2(\cos\beta) = \frac{1}{2}\left(3\cos^2\beta - 1\right) \tag{2}$$

and

$$P_4(\cos\beta) = \frac{1}{8}\left(35\cos^4\beta - 30\cos^2\beta + 3\right). \tag{3}$$

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*Corresponding author. Email: helen.gleeson@manchester.ac.uk

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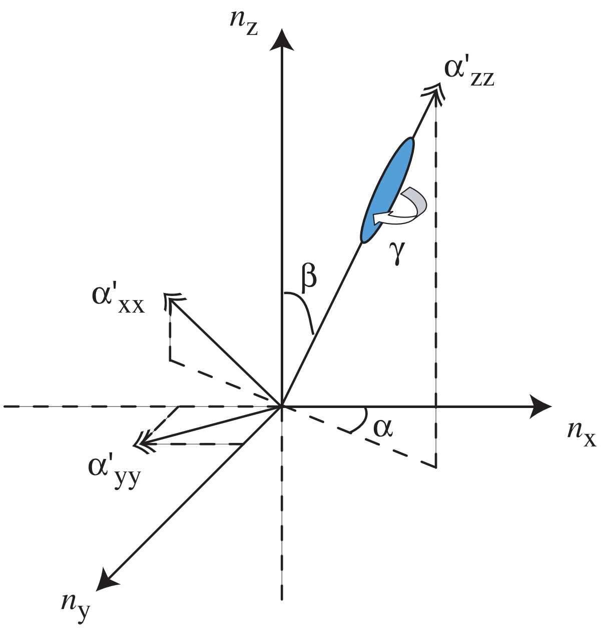

Figure 1. The rotational degrees of freedom of a uniaxial molecule in a nematic liquid crystal phase and the Euler angles, α, β and γ, relating the molecular and laboratory frames.

The calculated order parameters, plotted as a function of the reduced temperature, T/T_{NI}, where T is the temperature and T_{NI} is the nematic-to-isotropic phase transition temperature, are shown in Figure 2.

In the calculations, λ is a fitting parameter which describes the ratio, $\langle u_4\rangle/\langle u_2\rangle$, where $\langle u_L\rangle = \sum_n \langle u_{LL:n}(r)\rangle$, the average of the expansion coefficients of the pair-potential over all intermolecular separations. It is perhaps easiest to see the role of $\langle u_{LL:n}(r)\rangle$, given that the pseudo-potential between a molecule and the director is given by

$$U = \sum_{L:n} \langle u_{LL:n}(r)\rangle \langle P_L(\cos\beta)\rangle P_L(\cos\beta). \qquad (4)$$

This theoretical description facilitates an understanding of the interactions governing the orientational and symmetry properties of the liquid crystal phase formed from a system of anisotropic molecules. It also allows the development of methods for quantitative measurement of the orientational order of liquid crystal phases.

In order to provide a quantitative description of the molecular organisation in a liquid crystal phase the components of the relevant distribution function must be determined. A nematic liquid crystal exhibits only orientational order and the appropriate orientational distribution function (ODF), $f(\alpha,\beta,\gamma)$, contains terms which describe the angular distribution of the director about a defined coordinate system (in which α, β and γ are the Euler angles relating the molecular and laboratory frames, see Figure 1). For a phase with uniaxial symmetry formed from cylindrically symmetrical molecules, the normalised ODF can be simplified to an expansion containing the set of Legendre polynomials:

$$f(\beta) = \frac{1}{8\pi^2} \sum_{L(even)} (2L+1)\langle P_L \cos\beta\rangle P_L \cos\beta. \qquad (5)$$

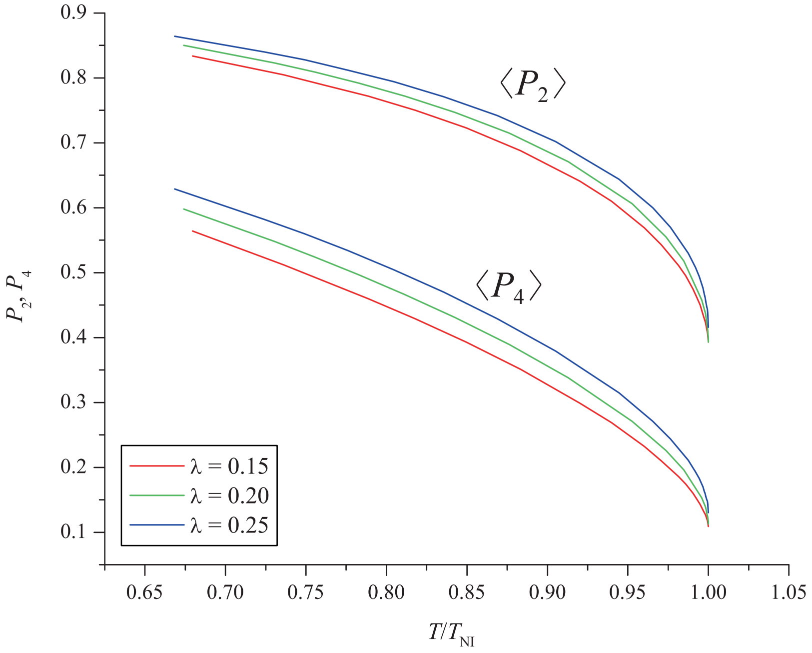

Figure 2. The calculated values of the order parameters $\langle P_2\rangle$and$\langle P_4\rangle$ as a function of the reduced temperature, T/T_{NI}. The different curves are for $\lambda = 0.15$, 0.20 and 0.25 (red, green and blue, respectively), where λ is the fitting parameter defined in the text (colour version online).

The tensorial properties of the anisotropic medium offer a means of determining the components of the ODF, and therefore allow quantification of the orientational ordering of the system. The many techniques available are described in various papers in this special volume, and here we concentrate only on optical methods for deducing the orientational order parameters.

2. Optical methods for determining orientational order parameters in uniaxial systems

2.1 Refractive indices

The anisotropy in liquid crystals results in the system exhibiting birefringence, and for a uniaxial nematic system this results in two measurable refractive indices, n_o and n_e, which are the refractive indices probed perpendicular to and along the director, respectively (also denoted by $n_\perp$ and $n_{||}$). In a nematic liquid crystal the birefringence is readily observed to increase with decreasing temperature, a consequence of the evolving order parameter, see Figure 3(a). In a uniaxial nematic phase the principal refractive indices can be expressed as

$$\frac{n_i^2-1}{n^2+2}=\frac{N\langle\sigma_{ii}\rangle}{3\varepsilon_0}, \tag{6}$$

where $\langle\sigma_{ii}\rangle$ is the average polarisability component along the principal refractive index direction, n_i, N is the number density, ε_o is the permittivity and n^2 denotes the square of the average refractive index of the system, $n^2=1/3\left(n_e^2+2n_o^2\right)$. The average polarisabilty along each of the principal axes is a function of both the polarisability anisotropy and the statistical orientation of the mesogenic molecules. Hence, for cylindrically symmetric molecules forming the uniaxial nematic phase, the second-rank polarisability tensor allows quantification of the first term in the ODF through measurement of the two principal refractive indices, $n_\perp$ and $n_{||}$, via

$$\frac{n_{||}^2-n_\perp^2}{n^2-1}=\frac{S\Delta\sigma}{\sigma}, \tag{7}$$

where $S=\langle P_2\cos\beta\rangle$, σ is the average polarisability and $\Delta\sigma=\left(\sigma_{||}-\sigma_\perp\right)$. The order parameter is extrapolated by assuming that its temperature dependence is of the form, $S=\left(1-\frac{T}{T_{\mathrm{NI}}}\right)^a$. A graph of $\log\left\{\frac{\left(n_{||}^2-n_\perp^2\right)}{\left(\bar{n}^2-1\right)}\right\}$ versus $\log\left(1-\frac{T}{T_{\mathrm{NI}}}\right)$ should be linear, with an intercept at absolute zero of the desired scaling factor, thus allowing the order parameter to be determined from refractive index measurements. The details of this technique have been described by Zeminder *et al.* [5].

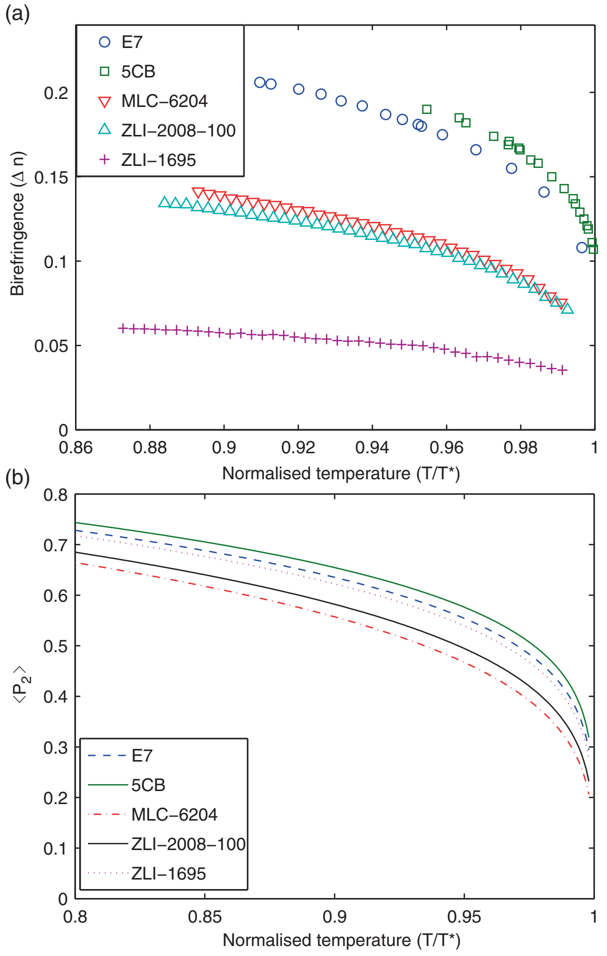

Figure 3. (a) Refractive index data and (b) the associated value of $\langle P_2\rangle$ for some typical nematogens, demonstrating the uniformity of value of the order parameter as a function of the reduced temperature, irrespective of the birefringence of the system. The parameter T^* is the nematic-to-isotropic transition temperature, and the uncertainty in deducing $\langle P_2\rangle$ is approximately 5%. All of the mixture names (E7, MLC–6204, ZLI–2008–100 and ZLI–1695) are as used by Merck Ltd, and 5CB is the nematogen 4-*n*-pentyl-4′-cyanobiphenyl (colour version online).

Refractive index measurements are usually carried out using an Abbé refractometer, a prism arrangement which contains the liquid crystal sample in a thin film between two prisms of high refractive index. The incident light undergoes total internal reflection for specific angles of incidence and polarisations; measurement of the critical angles allows the parallel and perpendicular components of the refractive index to be determined. It is important that the liquid crystal sample is uniformly aligned, producing a well-defined geometry for accurate measurements to be achieved. This technique readily gives measurements of the order parameter, $\langle P_2\rangle$, in nematic liquid crystals, see Figure 3(b). This has the merit of being simple and relatively accurate. However, the method assumes a straightforward relationship between the polarisability and the permittivity (i.e. the refractive index at optical frequencies). For anisotropic systems, however, this relationship is not straightforward, as the internal field experienced by a molecule is the sum of the macroscopic field and an average neighbouring field. Vuk's approximation, used here, is simple but assumes an isotropic internal field, necessarily leading to some error. There are also experimentally-related limitations to this methodology. The operating temperature range of most Abbé refractometers is limited to below 100°C due to the optical components in direct contact with the liquid crystal. It is also necessary to align the liquid crystal sample to obtain sufficiently accurate measurements of each of the refractive indices; since the liquid crystal sample is a bulk sample (several tens of microns across) this can be difficult to achieve.

There are many examples in the literature of the use of refractive index anisotropy to determine order parameters. Most recently this method has been used to determine orientational order parameters in the induced $\mathrm{SmA_d}$ phase [6], and to examine the critical behaviour at the isotropic–nematic and nematic–smectic A phase transitions [7]. It has also been used successfully for examining changes in order caused by the inclusion of photochromic dyes in a nematic mixture, although in this case it was not possible to measure any photo-induced changes in order [8]. Figure 3 shows both the refractive index data and the associated order parameters calculated for some typical nematogens which exhibit a wide variation in birefringence. It can be seen from Figure 3 that, as indicated, only $\langle P_2 \rangle$ is available, and we now move on to consider an optical methodology which also allows the determination of $\langle P_4 \rangle$.

2.2 *Polarised Raman spectroscopy*

Polarised Raman scattering spectroscopy (PRS) has the potential to be extremely powerful in probing the orientational order of liquid crystals. Raman scattering is the inelastic scattering of light from the rotational and vibrational modes of molecules; significant work has been published regarding the characteristics of the particular Raman active modes of mesogenic molecules. In particular, it has long been recognized that measurement of the anisotropy of the Raman scattered light can allow the measurement of the order parameters, $\langle P_2 \rangle$ and $\langle P_4 \rangle$. Indeed, along with X-ray scattering [9, 10], neutron scattering [11] and ESR spectroscopy [12], it is one of the few techniques which allows information to be gathered on the higher rank order parameters.

Typical measurements of the Raman spectrum of the liquid crystal 4-*n*-octyl-4′-cyanobiphenyl (8CB) are shown in Figure 4, for orientations of the light parallel and perpendicular to the director of the sample. The anisotropy in the scattering intensity is clear.

The seminal work of Jen *et al.* [13] has comprehensively demonstrated the measurement of uniaxial order parameters in 4′ methoxybentylidene 4-butylariline (MBBA) by means of the depolarisation ratios, and this work has found wide application by others [14–18]. In this section we review how the two uniaxial order parameters, $\langle P_2 \rangle$and$\langle P_4 \rangle$, are determined and extend the treatment to show how it is possible, in principle, to determine biaxial order parameters in nematic liquid crystals using PRS.

The scattered intensity of light re-radiated from a material is proportional to the square of the induced

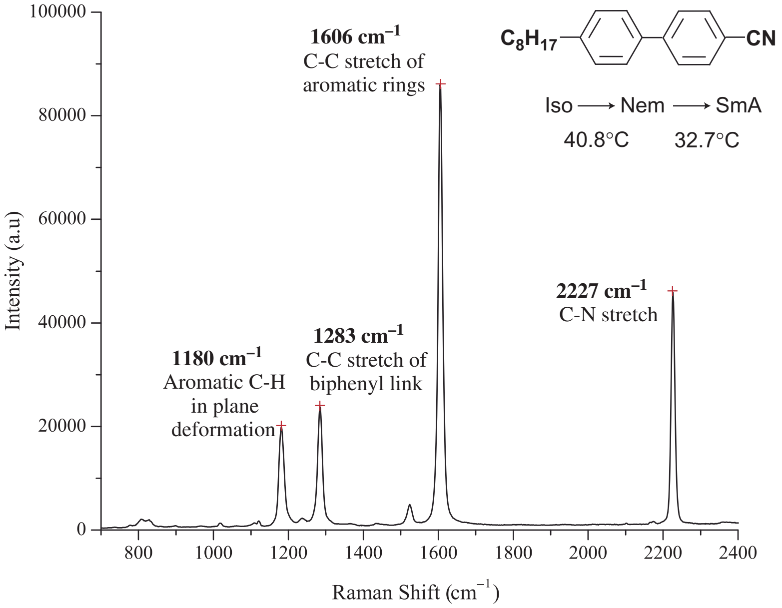

Figure 4. Raman spectra measured for 8CB (shown inset) for parallel and perpendicular orientations of the director with respect to the incident and scattered light.

dipole moment and, for Raman scattered light, is proportional to the square of the differential polarisability, $I \propto \left[\left(\frac{\partial\alpha}{\partial q_k}\right)_{q_k=0}\right]^2$. Since the molecular vibrational bands are anisotropic in a liquid crystalline medium, the scattered intensity can be used to deduce the ordering of the system. The approach has been described elsewhere [16, 17]. Briefly, the scattering from a molecule can be expressed by transforming the differential polarisability tensor (with derivatives along the primary axes of the molecule defined as α'_{xx}, α'_{yy} and α'_{zz}) into a particular frame of reference by expressing the scattering as a function of the Euler angles and the incident polarisation direction of the light with respect to θ. It is most convenient to define two orthogonal geometries where the coordinate axes lie parallel and perpendicular to the director, a planar cell geometry (with the molecular director in the plane of incidence) and a homeotropic cell geometry (with the molecular director perpendicular to the plane of incidence), respectively. As the observed intensity is simply proportional to the square of the electric field contributions for each of the geometries, and these contributions are further governed by the orientational distribution function (ODF), it can be seen that the observed intensity is of the form [16, 17]

$$I_{j,i}(\theta) = I_o \int_\alpha \int_\beta \int_\gamma f(\alpha,\beta,\gamma)\left(E_{j,i}(\alpha,\beta,\gamma)\right)^2 d\alpha d\beta\, d\gamma. \quad (8)$$

The subscripts, *i* and *j*, define the orientation of the polariser and analyser with respect to the director of the monodomain liquid crystal sample. Experimentally, the ODF can only be approximated by expressing the exact function as a Fourier transform in terms of the Wigner rotation matrices [19]. The rank of the tensorial properties monitored by an experiment dictate the measurable order parameters, and therefore the limit to which the ODF need be expanded. Since the Raman intensity is proportional to the square of the second-rank differential polarisability tensor, the measurement is actually of the second- and fourth-rank functions. The full expansion would yield a total of 34 terms but, as is to be expected, the symmetry of the system allows the expansion to be simplified. A useful discussion of the symmetry relations is reported by van Gurp [19] and by Zannoni [20]. These can be summarized as follows for a non-polar non-chiral nematic system:

- The system is symmetric with respect to a 180° rotation, restricting any expansions to even values only;
- In general, measurements of Raman bands are uniaxially symmetric, hence the measurement is not sensitive to any terms associated with a rotation about the Euler angle γ; and
- The sample is assumed to have mirror symmetry in the *xz*, *yz* and *xy* planes.

The observable order parameters are then reduced to the averages of generalised Legendre polynomials:

$$\begin{aligned}
P_{200} &= \frac{1}{2}\left(3\cos^2\beta - 1\right),\\
P_{220} &= \frac{1}{4}\left(1 - \cos^2\beta\right)\cos 2\alpha,\\
P_{400} &= \frac{1}{8}\left(3 - 30\cos^2\beta + 35\cos^4\beta\right),\\
P_{420} &= \frac{1}{24}\left(-1 + 8\cos^2\beta - 7\cos^4\beta\right)\cos 2\alpha,\\
P_{440} &= \frac{1}{16}\left(1 - 2\cos^2\beta - \cos^4\beta\right)\cos 4\alpha. \qquad (9)
\end{aligned}$$

The notation is such that the subscripts *L, m* and *n* in $P_{L,m,n}$ represent the conditions under rotations of α, β and γ, respectively, and a consequence of the symmetry is that *L*, *m* and *n* must have even values. Furthermore, the Raman bands themselves generally have uniaxial symmetry, i.e. $\alpha_{zz} > \alpha_{xx}(= \alpha_{yy})$, so that all order parameters associated with a rotation about γ are zero, and therefore only terms with $n = 0$ are non-zero in this approach. These expressions allow the ODF to be expressed up to fourth-order contributions [19],

$$\begin{aligned}
f(\alpha,\beta) =& \frac{1}{8\pi}\Big[1 + \frac{5}{2}\langle P_{200}\rangle(3\cos^2\beta - 1)\\
&+ 15\langle P_{220}\rangle\left(1 - \cos^2\beta\right)\cos 2\alpha\\
&+ \frac{9}{8}\langle P_{400}\rangle\left(3 - 30\cos^2\beta + 35\cos^4\beta\right)\\
&+ \frac{135}{2}\langle P_{420}\rangle\left(-1 + 8\cos^2\beta - 7\cos^4\beta\right)\cos 2\alpha\\
&+ \frac{315}{4}\langle P_{440}\rangle\left(1 - 2\cos^2\beta + \cos^4\beta\right)\cos 4\alpha\Big].
\end{aligned} \qquad (10)$$

In addition to allowing the conventional uniaxial order parameters $\langle P_{200}\rangle$ and $\langle P_{400}\rangle$ to be determined, these functions in principle also show that some of the order parameters associated with biaxality can be determined. The most robust way of determining any such order parameters is to consider the integral Equation (8) and to fit the Raman scattering intensity for specific bands, determined as a function of angle of the incident polarisation vector, related to Equations (11) and (12):

$$I_{||}(\theta) = I_0 \int_{\alpha,\beta,\gamma} f(\beta)\big(E_{||}(\alpha,\beta,\gamma,\theta)\big)^2 d\alpha d \sin\beta d\gamma, \quad (11)$$

$$I_{\perp}(\theta) = I_0 \int_{\alpha,\beta,\gamma} f(\beta)(E_{\perp}(\alpha,\beta,\gamma,\theta))^2 d\alpha d \sin\beta d\gamma. \quad (12)$$

However, it is noteworthy that past practice has generally relied on measurements of the depolarisation ratio, $R(\theta) = \frac{I_{\perp}(\theta)}{I_{||}(\theta)}$, only at specific values of θ rather than for the whole angular range, together with an assumption that one of the critical parameters relied on in the usual simplifications, r, is constant at all temperatures and hence can be determined simply in the isotropic phase, where by definition all the orientational order parameters are zero. This approach has been used to determine some of the order parameters in nematic liquid crystals quite successfully and, in addition, measurements of the depolarisation ratio R have been exploited to determine some of the more subtle smectic phase transitions. However, while using the simplified approach gives reasonable values for $\langle P_{200}\rangle$ it has not given reliable results for $\langle P_{400}\rangle$, in some cases even returning negative values. We have discussed this phenomenon in [21], and will consider it in more detail in the sections following.

2.3 Experimental measurements of order parameters using PRS

This section focuses on measurements of the orientational order parameters for bent-core nematogens, systems of considerable interest due to their potential for exhibiting the elusive biaxial nematic phase. However, data are presented initially for a uniaxial system, 8CB, to demonstrate the effectiveness of determining the full angular distribution of the depolarisation ratio in Raman scattering to measure the order parameters [21]. Importantly, this approach also allows the differential polarisability parameter, r, to be a variable rather than a constant (a common assumption in previous work), in order to measure $\langle P_{200}\rangle$ and $\langle P_{400}\rangle$ effectively, resulting in values that offer good agreement with theory. This approach demonstrates that previous anomalous measurements of $\langle P_{400}\rangle$ (including cases where it appeared to take a negative value) are a consequence of assuming that the differential polarisability, r, is a constant that can be determined in the isotropic phase, whereas its value strongly depends in fact on both the phase and temperature of the system.

In all of the measurements described in this review article we have used a Renishaw 1000 Raman microscope to determine the Raman spectra. The system is designed to guide a polarised laser beam into a polarising microscope and focus it on the prepared sample. A significant advantage of this arrangement is that the liquid crystal sample can be held in a conventional hot stage and the texture viewed, ensuring that measurements are made only in areas of uniform alignment. The scattered laser light passes through a series of holographic notch filters, which remove the Rayleigh scattered portion of the light before reaching the analyser. This light is spectrally resolved and falls on a charge-coupled detector which measures the intensity of the Raman light. The laser source is an argon-ion laser operating at 514 nm, and a power of around 10 mW is used to illuminate the sample; this power is reduced considerably by the optical system before it is incident on the liquid crystal. The incident laser polarisation ratio is 1 : 100 and is focused on to the sample by a 50 × long working distance objective lens. The system allows for a resolution of 0.5 cm^{-1} in the Raman-shifted light. The apparatus has been designed to minimize the effect of instrumental parameters on the polarisation state of the incident and scattered light [22], since such factors can contribute as much as 8% to the measured Raman intensities. Our choice of back-scattered geometry, together with the use of the 50 × objective lens (numerical aperture = 0.55), has been shown to have a negligible effect on the polarisation state of the light, an important consideration for the measurements considered here.

The measured depolarisation ratio for the phenyl-stretching mode of 8CB is shown in Figure 5(a), together with the line of best fit to the data. This fit allows extraction of the parameters $\langle P_{200}\rangle$, $\langle P_{400}\rangle$ and r, which take values of 0.42 ± 0.05, 0.21 ± 0.05 and –0.150 $\pm$ 0.015, respectively, at a temperature of 38°C. These values are in excellent agreement with those of Jones *et al.* [16, 17]. If we follow the approach of analysing the data obtained only for two specific points, as is quite common in the published literature, the value of $\langle P_{200}\rangle$ does not change significantly, but that for $\langle P_{400}\rangle$ is reduced by a factor of around 2, offering very poor agreement with theory, in contrast to the approach followed here (see Figure 5(b)) [21].

The fitting procedure followed in our work has built on that published by Jones *et al.* [16, 17]. A χ^2 minimization fitting routine was applied to the depolarisation ratio with $\langle P_{200}\rangle$, $\langle P_{400}\rangle$ and r as fitting parameters. The solid line in Figure 5(a) shows the best fit, which reproduces all of the characteristic features observed experimentally. The difference between the value of r measured in the isotropic phase and the value deduced from the fit is quite significant, particularly in determining the value of $\langle P_{400}\rangle$ [23]. Indeed, it is clear from our investigations that the assumption that r is constant and can be measured in the isotropic phase is the source of the reported measurements of $\langle P_{400}\rangle$ that are much lower than predicted by theory.

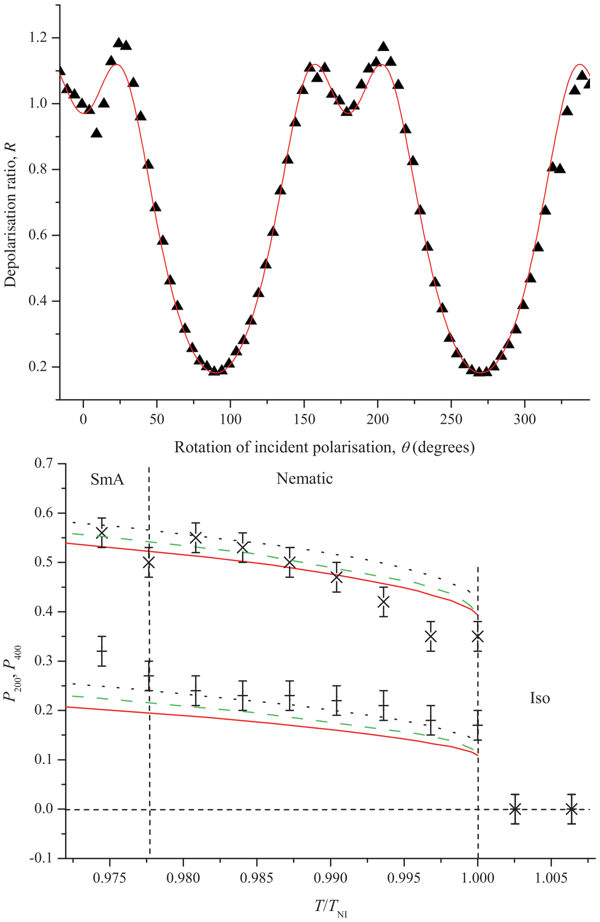

Figure 5. (a) The experimentally measured depolarisation ratio for 8CB at a temperature of 38°C, together with the best fit profile for the data, and (b) the order parameters $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$deduced for the data across the nematic temperature regime together with theoretically generated data with values of $\lambda = 0.15$ (solid red line); $\lambda = 0.20$ (green dashed line); and $\lambda = 0.25$ (dotted black line). It is seen that this provides a robust method for measuring both $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$, yielding values of each in excellent agreement with theory (colour version online).

2.4 Measurements of order parameters in bent-core nematic materials

The first bent-core molecules reported to exhibit liquid crystal phases were produced by Vorländer in 1929 [24], work which was not followed up until 1991 when Matsunaga *et al.* [25] synthesized a number of bent-core materials, leading to the discovery of a set of liquid crystal phases (the B-phases, or banana phases) unique to systems with this geometry. More recently, nematic liquid crystalline phases formed from bent-core materials generated huge excitement when, in 2004, they were reported to exhibit biaxial order [26, 27]. We were motivated by the potential for measuring the biaxial order parameters in bent-core nematic liquid crystal materials using PRS, taking advantage of the fitting procedure to deduce the various order parameters.

The existence of biaxial ordering in a nematic liquid crystal phase is crucially dependent on the presence of molecular biaxiality. Consequently it is important to consider both the molecular symmetry and how this symmetry is reflected in the probe used to infer the ordering of the system. In determining the biaxiality experimentally there are two possible scenarios; either using an individual biaxial probe, or alternatively using a collection of probes forming a biaxial unit. It is the latter approach that is used for bent-core molecules, where the distribution of potential Raman probe groups can be used to model a biaxial unit. The molecular biaxiality is defined by the molecular bend angle, Ω, defined in Figure 6.

For the molecules we have considered, we have examined two independent scattering units (the phenyl stretch mode), each positioned along one of the molecular arms. Assuming that the scattering units are independent, the intensity can be described by summing the electric field contributions from each arm,

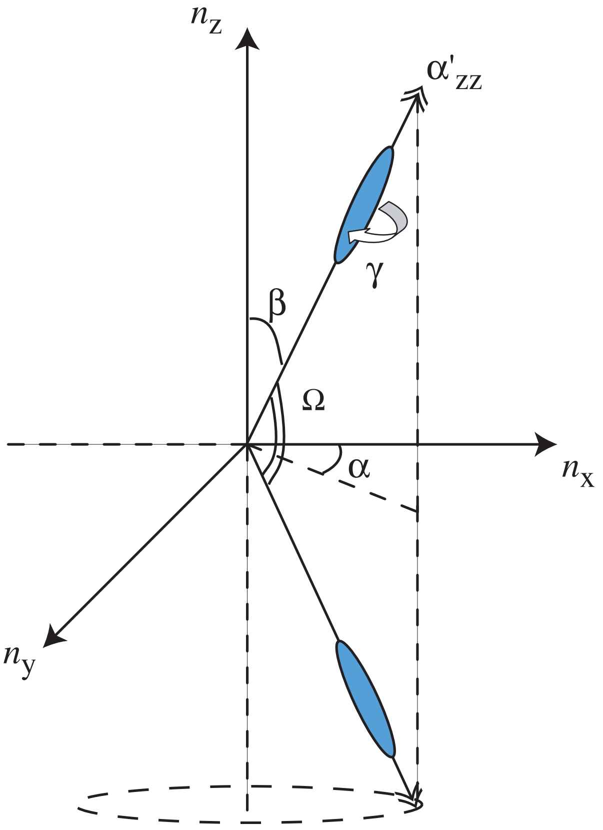

Figure 6. A schematic of the model employed for the bent-core molecules used in this study, showing the rotational degrees of freedom. Each of the molecular arms contains an independent scattering unit. This model is important, whether determining order parameters in either the uniaxial or biaxial phases. The bend angle is defined by the parameter Ω, while α, β, and γ shown are the Euler angles given in Figure 1 .

$$I_{||}(\theta) = I_0 \int_\alpha \int_\beta \int_\gamma f(\alpha,\beta,\gamma)\left(E_{||}^{Arm1}(\alpha,\beta,\gamma,\Omega) + E_{||}^{Arm2}(\alpha,\beta,\gamma,\Omega)\right)^2 d\alpha d\sin\beta d\gamma,$$

$$I_{\perp}(\theta) = I_0 \int_\alpha \int_\beta \int_\gamma f(\alpha,\beta,\gamma)\left(E_{\perp}^{Arm1}(\alpha,\beta,\gamma,\Omega) + E_{\perp}^{Arm2}(\alpha,\beta,\gamma,\Omega)\right)^2 d\alpha d\sin\beta d\gamma,$$

where in each case the angles are those defined previously.

The presence of phase biaxiality is defined by the symmetry breaking associated with a hindered rotation about the Euler angle, α, and consequently the order parameters describing a two-fold rotational symmetry about α (reflected by $|m| = 0, 2, 4$). Provided a uniaxial Raman active mode is used, so that the molecular biaxiality is defined by the bend angle, the orientational distribution function, Ω, can be expressed as a function of α and β only, see Equation (8). In the definition of $f(\alpha, \beta)$, $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ are uniaxial order parameters, while $\langle P_{220} \rangle$, $\langle P_{420} \rangle$ and$\langle P_{440} \rangle$ define the phase biaxiality. In order to measure all of the order parameters by the fitting technique, it is important to note that there are now five order parameters, with the differential polarisability parameter, r, and the molecular bend angle, Ω, as fitting parameters. It is, therefore, clear that it is necessary to consider additional experimental geometries to reduce the potential for degeneracy in the fits if the order is to be properly determined. This is difficult in the bent-core molecules, since for the systems we have studied [23], it has been impossible to date to obtain good homeotropic alignment. This approach has nonetheless been used, together with small-angle X-ray scattering to allow us to report all of the order parameters in compound **d** shown in Figure 7 [28], in which both data sets indicated a uniaxial-to-biaxial nematic transition around 35°C below the nematic-to-isotropic transition temperature.

Although using the approach of fitting to the depolarisation ratio can, due to degeneracy, be problematic in determining experimentally biaxial order parameters, it is, nonetheless, possible to model the expected depolarisation ratio for different values of $\langle P_{200} \rangle$, $\langle P_{400} \rangle$, $\langle P_{220} \rangle$, $\langle P_{420} \rangle$ and$\langle P_{440} \rangle$. This is demonstrated in Figure 8, which shows how the depolarisation ratio, measured for a sample with planar alignment, varies for differing degrees of phase biaxiality. In Figure 8(a) there is assumed to be no biaxial order and the effect of adding biaxial terms appears to squash the profile. The dominant biaxial term is $\langle P_{220} \rangle$ which, when taking non-zero values, appears

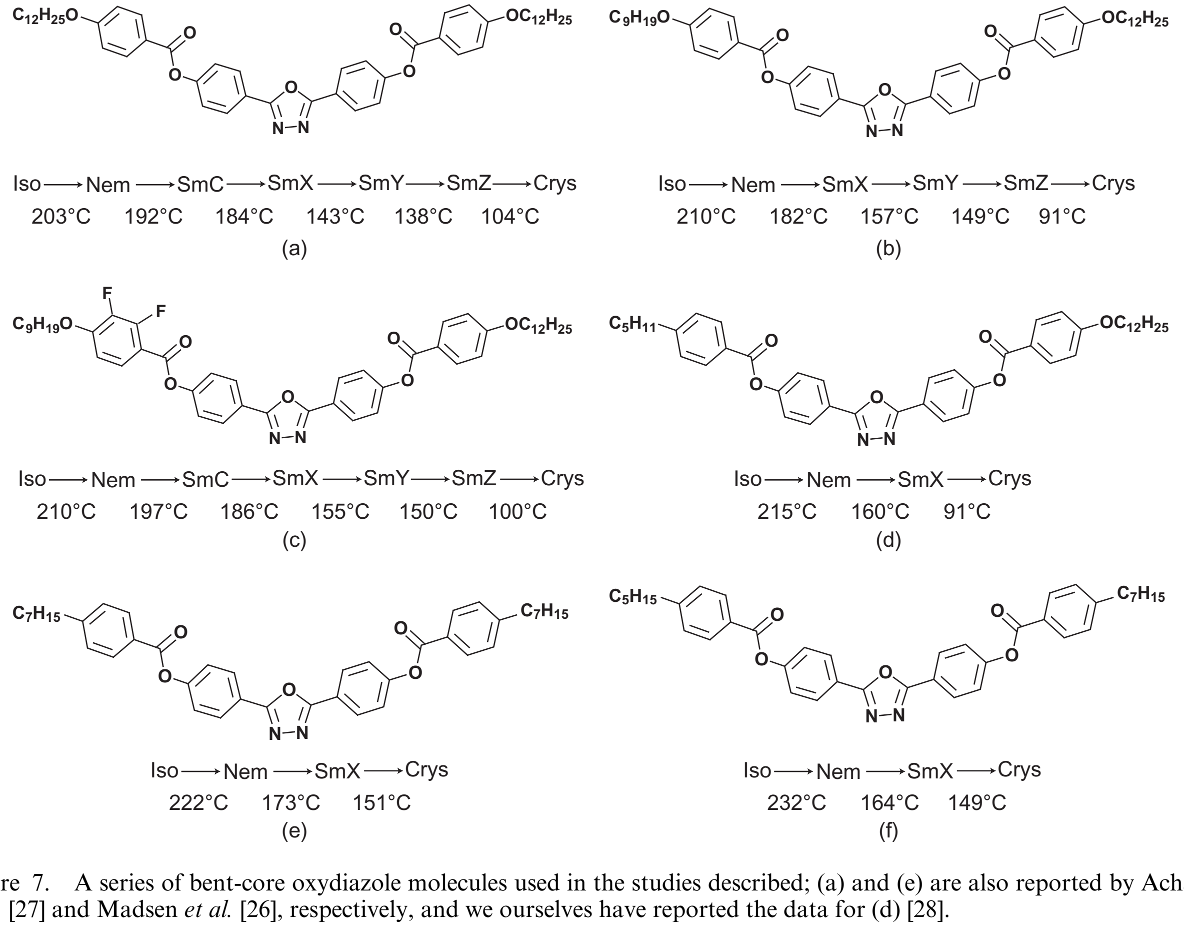

Figure 7. A series of bent-core oxydiazole molecules used in the studies described; (a) and (e) are also reported by Achayra *et al.* [27] and Madsen *et al.* [26], respectively, and we ourselves have reported the data for (d) [28].

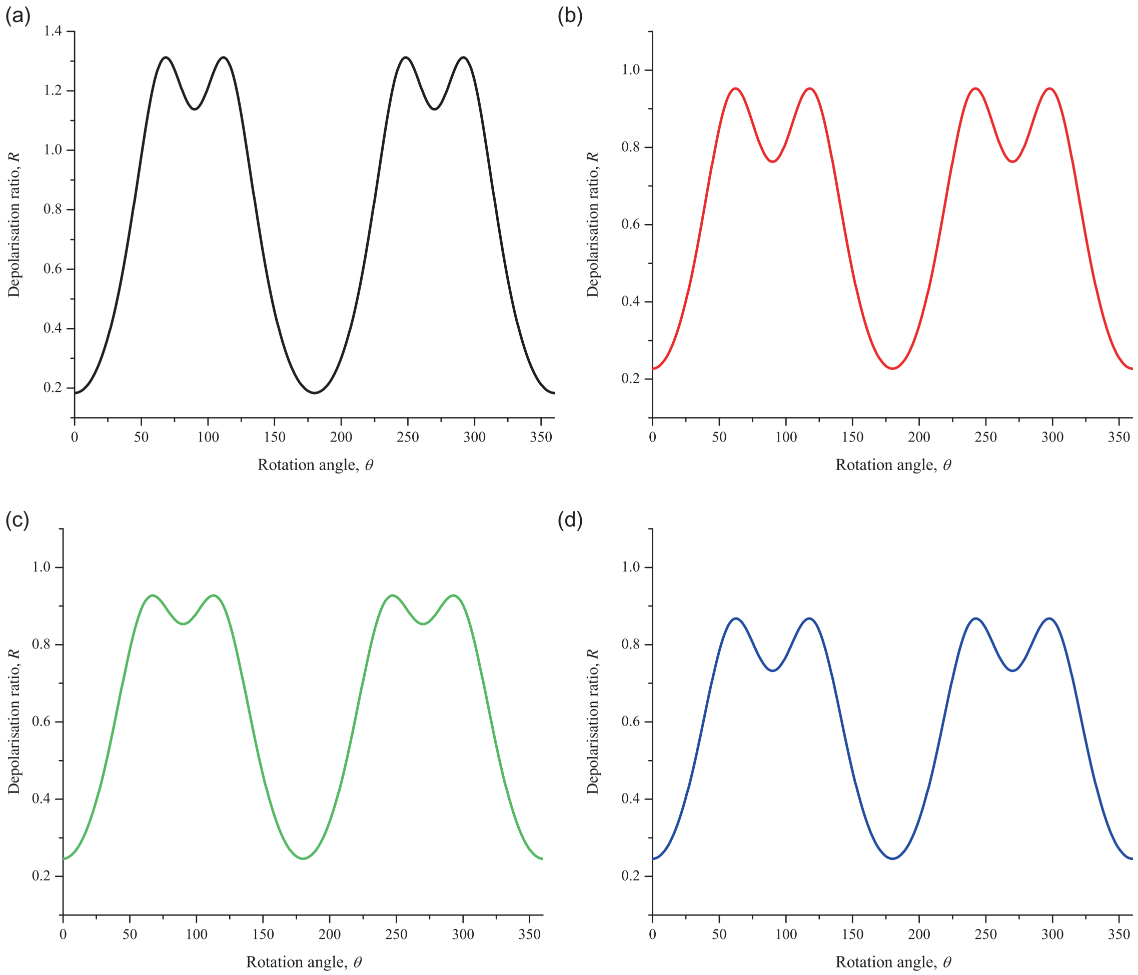

Figure 8. The modelled depolarisation ratio, *R*, for varying degrees of assumed phase biaxiality; (a) $\langle P_{200}\rangle = 0.53$, $\langle P_{400}\rangle = 0.23$, $\langle P_{220}\rangle = \langle P_{420}\rangle = \langle P_{440}\rangle = 0$; (b) $\langle P_{200}\rangle = 0.53$, $\langle P_{400}\rangle = 0.23$, $\langle P_{220}\rangle = 0.12$, $\langle P_{420}\rangle = 0$ and $\langle P_{440}\rangle = 0$; (c) $\langle P_{200}\rangle = 0.53$, $\langle P_{400}\rangle = 0.23$, $\langle P_{220}\rangle = 0.12$, $\langle P_{420}\rangle = 0.08$ and $\langle P_{440}\rangle = 0$; and (d) $\langle P_{200}\rangle = 0.53$, $\langle P_{400}\rangle = 0.23$, $\langle P_{220}\rangle = 0.12$, $\langle P_{420}\rangle = 0.08$ and $\langle P_{440}\rangle = 0.08$.

to decrease significantly the peak-to-peak amplitude of the depolarisation ratio (see Figure 8(c)). The two fourth-rank contributions, $\langle P_{420}\rangle$ and $\langle P_{440}\rangle$, influence different parts of the distribution; $\langle P_{420}\rangle$ increases the minima around 0° and 180° while reducing the oscillatory feature around 90° and 270°, whereas $\langle P_{440}\rangle$ only affects the oscillatory feature. The influence of each is sufficient that, provided the degeneracy can be broken by providing additional information, it should be possible to use this approach effectively in determining the biaxial order parameters in bent-core systems.

While there are too many fitting parameters to determine effectively the biaxial order parameters (if they exist) in all six of the oxadiazole bent-core molecules shown in Figure 7, it has nonetheless proven possible to determine the uniaxial order across the nematic range by assuming no biaxiality, i.e. fitting only for $\langle P_{200}\rangle$, $\langle P_{400}\rangle$ and *r*. In all cases, the experimental approach was as described previously, and the C–C stretch of the aromatic rings at 1606 cm^{-1} was used as the Raman probe (this is the strongest scattering peak for the bent-core molecules). While neglecting any possible contribution from the biaxial order will clearly increase uncertainty, this additional assumption does not significantly affect the uncertainty in determining the uniaxial order parameters, which is around ±0.05 [23], and these data are presented in Figure 9. A similar experimental approach has been used to study the de Vries SmC* phase [29] and has recently [30] allowed the order parameters in a series of smectic-A materials with transitions to tilted phases to be examined, in that case differentiating unequivocally between the SmC*$_a$ phase and a de Vries SmC* phase. Polarised Raman Scattering has also been effectively used to determine changes in biaxiality in an anti-ferroelectric system [31], although the biaxiality was inferred from the anomalous behaviour of the $\langle P_4\rangle$ order parameter rather than by introducing biaxial terms in the analysis. The potential for measuring order parameters in a variety of liquid crystalline systems is clear.

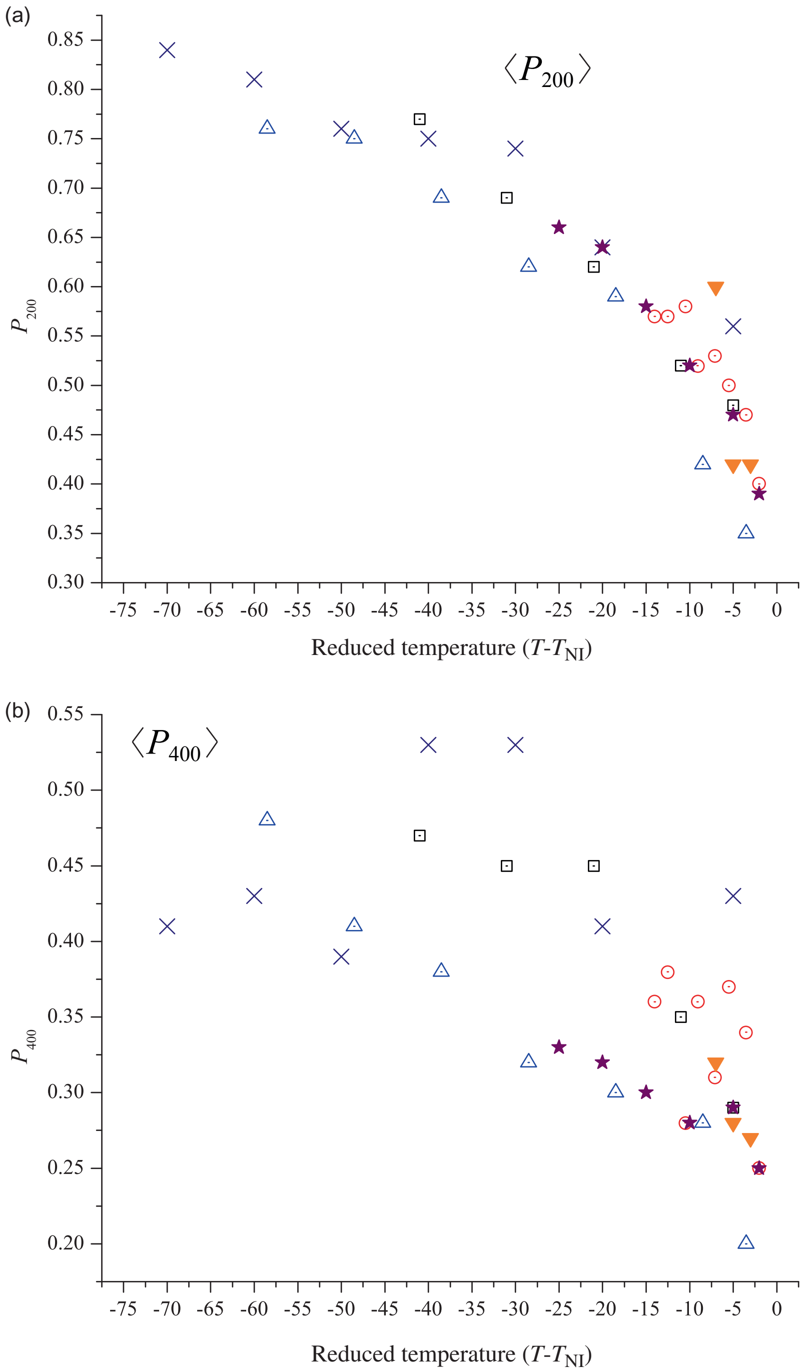

Figure 9. The uniaxial order parameters $\langle P_{200}\rangle$ and $\langle P_{400}\rangle$ determined for the oxidiazole systems described in Figure 7. The uncertainties in all cases are ±0.05. The molecules in Figure 7 are described by the symbols as (a) orange triangle, (b) purple star, (c) red circle, (d) blue triangle, (e) blue square and (f) blue cross; (a) and (e) are also reported by Achayra *et al.* [27] and Madsen *et al.* [26], respectively, and we ourselves have reported the data for (d) [28] (colour version online).

3. Summary

This review has outlined the importance of using optical techniques to determine orientational order parameters in nematic liquid crystals. New data have been presented for $\langle P_{200}\rangle$ deduced for a variety of nematogens with very different refractive indices, and for both $\langle P_{200}\rangle$ and $\langle P_{400}\rangle$ for a series of bent-core oxydiazoles. It is clear that Polarised Raman Scattering offers a very promising technique for determining biaxial order parameters in nematic liquid crystals, as the depolarisation ratio data generated for specific values of the different possible uniaxial and biaxial order parameters demonstrate. This experimental approach is complementary to other techniques such as NMR and polarised IR measurements. It probes the same biaxial order parameters as NMR, but does so without the presence of the high magnetic fields necessary for NMR. The samples used in Raman scattering can be held in standard liquid crystal devices with glass substrates (although for the systems considered here it was important to use very high temperature alignment layers and glue) whereas for polarised IR measurements specialised substrates are required. Further, the use of the Raman microscope for the measurements presented here ensures that only well-aligned areas are considered as the sample quality is readily evaluated via polarising microscopy. In summary, the use of PRS in studying biaxiality in liquid crystals has considerable promise as an additional technique which can contribute to a full understanding of biaxial order in liquid crystal systems. Nonetheless, in order to fully exploit this method of probing biaxiality in the future, it will be necessary to probe more than one sample geometry, thereby removing the degeneracy that is inherent in fitting such a large number of variables (some of which are related) to a single set of experimental data. We will report on such measurements for the biaxial smectic-A phase shortly.

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References

[1] Maier, W.; Saupe, A. *Z. Naturforsch.* **1958**, *13a*, 564–556.
[2] Chandrasekhar, S.; Krishnamurti, D.; Madhusudana, N.V. *Mol. Cryst. Liq. Cryst.* **1969**, *8*, 45–69.
[3] Chandrasekhar, S.; Madhusudana, N.V. *Acta Cryst.* **1971**, *27*, 303–313.
[4] Humphries, R.L.; James, P.G.; Luckhurst, G.R. *J. Chem. Soc., Faraday Trans 2* **1972**, *68*, 1031–1044.
[5] Zeminder, A.K.; Paul, S.; Paul, R. *Mol. Cryst. Liq. Cryst.* **1980**, *61*, 191–205.
[6] Roy, P.D.; Prasad, A.; Das, M.K. *J. Phys.: Condens. Matter* **2009**, *21*, 075106.
[7] Yildiz, S.; Ozbek, H.; Glorieux, C.; Thoen, J. *Liq. Cryst.* **2007**, *34*, 611–620.
[8] Allinson, H.; Gleeson, H.F. *Liq. Cryst.* **1993**, *14*, 1496–1478.
[9] Leadbetter, A.J.; Norris, E.K. *Mol. Phys.* **1979**, *38*, 669–686.
[10] Deutsch, M. *Phys. Rev. A: At., Mol., Opt. Phys.* **1991**, *44*, 8264–8270.
[11] Richardson, R.M.; Allman, J.M.; McIntyre, G.J. *Liq. Cryst.* **1990**, *7*, 701–719.
[12] Luckhurst, G.R.; Yeates, R.N. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 996–1009.
[13] Jen, S.; Clark, N.A.; Pershan, P.S.; Priestley, E.B. *Phys. Rev. Lett.* **1973**, *31*, 1552–1556; *J. Chem. Phys.* **1977**, *66*, 4635–4661.
[14] Bauman, D.; Chrzumnicka, E.; Mykowska, E.; Szybowicz, M.; Grzelczak, N. *J. Mol. Struct.* **2005**, *744*, 307–313.
[15] Hayashi, N.; Kato, T.; Fukuda, A.; Vij, J.K.; Panarin, Y.P.; Naciri, J.; Shashidhar, R.; Kawada, S.; Kondoh, S. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2005**, *71*, 041705.
[16] Jones, W.J.; Thomas, D.K.; Thomas, D.W.; Williams, G. *J. Mol. Struct.* **2004**, *708*, 145–163.
[17] Jones, W.J.; Thomas, D.K.; Thomas, D.W.; Williams, G. *J. Mol. Struct.* **2002**, *614*, 75–85.
[18] Davies, A.N.; Jones, W.J.; Price, A.H. *J. Raman Spectrosc.* **1994**, *25*, 521–529.
[19] van Gurp, M. *Colloid. Polym. Sci.* **1995**, *273*, 607–625.
[20] Zannoni, C. In *The Molecular Physics of Liquid Crystals*: Luckhurst, G.R., Gray, G.W., Eds.; Academic Press: London, 1979.
[21] Southern, C.; Gleeson, H.F. *Eur. Phys. J. E* **2007**, *24*, 119–127.
[22] Tanaka, M.; Young, R.J. *J. Mater. Sci.* **2006**, *41*, 963–991.
[23] Southern, C. Ph.D. Dissertation, University of Manchester, UK, 2008.
[24] Vorländer, D. *Ber. Deutsche Chem. Ges.* **1929**, *62*, 2831–2835.
[25] Kuboshita, M.; Matsunaga, Y.; Matsuzaki, H. *Mol. Cryst. Liq. Cryst.* **1991**, *199*, 319–326.
[26] Madsen, L.A.; Dingemans, T.J.; Nakata, N.; Samulski, E.T. *Phys. Rev. Lett.* **2004**, *92*, 145505.
[27] Acharya, B.R.; Primak, A.; Kumar, S. *Phys. Rev. Lett.* **2004**, *92*, 145506.
[28] Southern, C.D.; Brimicombe, P.D.; Siemianowski, S.D.; Jaradat, S.; Roberts, N.; Görtz, V.; Goodby, J.W.; Gleeson, H.F. *Eur. Phys. Lett.* **2008**, *82*, 56001.
[29] Hayashi, N.; Kato, T.; Fukuda, A.; Vij, J.K.; Panarin, Y.P.; Naciri, J.; Shashidhar, R.; Kawanda, S.; Kondo, S. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2005**, *71*, 041705.
[30] Chang, H.-S.; Jaradat, S.; Gleeson, H.F.; Dierking, I.; Osipov, M. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2009**, *79*, 061706.
[31] Hayashi, N.; Kato, T. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2001**, *63*, 021706.