X-ray diffraction from the uniaxial and biaxial nematic phases of bent-core mesogens

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X-ray diffraction patterns for the uniaxial and biaxial nematic phases exhibited by rigid bent-core mesogens were calculated using a simple model for the molecular form factor and a modified Lorentzian structure factor. The X-ray diffraction patterns depend strongly on the extent of the alignment of the molecular axes as well as the orientation of molecular planes. The X-ray diffraction can be unequivocally used to identify the biaxial nematic phase, study the uniaxial–biaxial phase transition, and estimate the order parameters of the nematic phase.

Keywords: X-ray diffraction; uniaxial–biaxial phase transition; biaxial nematic phase; bent-core mesogen

1. Introduction

X-ray diffraction (XRD) has been widely used for phase identification (*1*), the study of phase transitions (*2–4*) and to extract structural information (*5*) of various liquid crystal (LC) phases. In a typical XRD experiment, the intermolecular correlations along the direction of the average molecular orientation, known as the director, **n**, are extracted form the quasi-Bragg peaks at small angle and the in-plane structural information is extracted from the distribution of the scattered intensity in the diffused crescents at large angles, corresponding to the intermolecular separation along the lateral direction. In general, the diffraction pattern from an isotropic liquid of rod-shaped molecules exhibits two diffused rings at small and large angles. For an aligned nematic, the two rings condense into two pairs of diffuse crescents along orthogonal directions. When the nematic phase is cooled into a (well-aligned) smectic A phase the two small-angle crescents of the nematic phase condense into two sharp quasi-Bragg peaks but the large-angle reflections remain essentially the same. Depending on the orientation of the smectic planes relative to the director, the smectic C (SmC) phase can have two or four quasi-Bragg peaks at small angle (*1*). The existence of four diffuse peaks in the XRD from the nematic phase of the rod-shaped molecules has been attributed to the pre-transitional fluctuations of the underlying SmC phase, also referred to as the cybotactic groups (*6*). The intensity distribution in the outer reflections of the nematic phase also has previously been exploited to extract the distribution function and the order parameter of the nematic phases of thermotropic LCs (*7*) and rod-shaped viruses (*8*).

With certain fundamental assumptions, the expression for the azimuthal intensity distribution can be solved analytically and inverted to yield the molecular orientational distribution function. The azimuthal distribution function can then be used to calculate the values of the relevant order parameters. In these calculations, the scattered intensity is approximated, in the small- or large-scattering vector regime, to extract information about the intramolecular or the interparticle scattering, respectively. The contribution from intraparticle scattering (i.e. the form factor) provides information about the molecular structure of the LCs and the interparticle scattering (i.e. the structure factor) provides information about positional correlations between the molecules.

As new molecular architectures emerge, conventional approximations used in the analysis of XRD patterns are not sufficient to fully describe the LC phases formed by these molecules. Recently, we have used the form factor and the structure factor to calculate the scattering intensity from an aligned monodomain nematic phase of bent-core molecules. The calculated X-ray intensity distribution exhibited distinct diffraction patterns in the two orthogonal directions in the plane perpendicular to the nematic director, **n**. Combined with the experimental results from oxadiazole-based rigid bent-core molecules, this led to the discovery of theoretically predicted but highly elusive biaxial nematic phase in a low molar mass thermotropic LCs (*9, 10*). This discovery was later confirmed by NMR experiments (*11*) and by atomistic simulations (*12*). In this paper, we present a detailed calculation of the evolution of the four diffuse peaks in the XRD pattern in bent-core

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molecules. Mayer–Saupe type single parameter distribution functions are used to describe the orientation of molecular axes and the planes of the bent-core molecules. These results, when combined with the experimental XRD, demonstrate that the bent-core molecules can exhibit both uniaxial and biaxial nematic phases and reveal the nature of the uniaxial–biaxial nematic phase transition.

This paper is organised as follows. First, we describe the basics of XRD from the nematic phase formed from the rod-like molecules and calculate the two-dimensional diffraction pattern. A comparison between the theoretically calculated diffraction pattern and the experimental data is made to validate results from theoretical calculations. Then, we induce a "bend" in the rod-like molecules to form a bent-core molecule and calculate the form factor and the scattered intensity. Next, we introduce the molecular distribution functions and vary the "order" parallel to the two orthogonal (primary and secondary) nematic directors. The calculated diffracted intensity profiles are finally compared with the recent results from the XRD experiments on bent-core compounds.

2. X-ray scattering from rod-like molecules

When an incoming radiation of wavelength λ is scattered from a volume V with electron density $\rho(r)$, the complex function describing the amplitude and the phase of the scattered wave is given by $f(\mathbf{q}) = \int_V \rho(\mathbf{r})\exp(\mathbf{q}.\mathbf{r})d\mathbf{r}$, where $\mathbf{q}$ is the scattering vector. The scattered intensity in $\mathbf{q}$-space is given by $I(\mathbf{q}) = f(\mathbf{q}) \times f^*(\mathbf{q})$, where $f^*(\mathbf{q})$ is the complex conjugate of $f(\mathbf{q})$. The scattering intensity from a molecule is given by summing over all the atoms on the molecule:

$$I(\mathbf{q}) = \sum_j f_j(\mathbf{q})\exp(i r_j.\mathbf{q}) \sum_k f_k(\mathbf{q})\exp(-i r_k.\mathbf{q})$$
$$= \sum_j \sum_k f_j(\mathbf{q})f_k(\mathbf{q})\exp\left[i(\mathbf{r}_j - \mathbf{r}_k).\mathbf{q}\right]. \quad (1)$$

For a system of N molecules, the total scattered intensity at a point in the $\mathbf{q}$-space is given by averaging over all the molecules and their orientations,

$$I(\mathbf{q}) = \left\langle \sum_j \sum_k f_j(\mathbf{q})f_k(\mathbf{q})\exp\left[i(\mathbf{r}_j - \mathbf{r}_k).\mathbf{q}\right] \right\rangle. \quad (2)$$

This expression can be decomposed into two terms: the form factor, $F(\mathbf{q})$, that depends on a single particle distribution function and the structure factor, $S(\mathbf{q})$, that includes the spatial and orientational correlations:

$$I(\mathbf{q}) = NF(\mathbf{q}) \times S(\mathbf{q}). \quad (3)$$

The form factor, $F(\mathbf{q})$, given by $F(\mathbf{q}) = <|f(\mathbf{q})|^2>$ is essentially the average of the modulus square of Fourier transform of the electron density. The structure factor depends on the relative positions and orientation of two neighbouring molecules and is given by (3):

$$S(\mathbf{q}) = 1 + \frac{1}{NF(\mathbf{q})}\left\langle \sum_{j \neq k} f_j(\mathbf{q})f_k(\mathbf{q})\exp\left[i(\mathbf{r}_j - \mathbf{r}_k).\mathbf{q}\right] \right\rangle. \quad (4)$$

Now for particles with spherical symmetry, the electronic density functions are independent of the orientations of the particles and $f_j(\mathbf{q}) = f_k(\mathbf{q})$, and the form factor and the structure factor decouple. For anisotropic shaped (e.g. rod-like or disc-like) molecules, $f_j(\mathbf{q}) \neq f_k(\mathbf{q})$ and the structure factor and the form factor do not decouple except when all the molecules are aligned parallel to each other. In general, XRD data are analysed by approximating the scattered intensity either by the form factor $F(\mathbf{q})$ alone in the high $\mathbf{q}$ limit, or with an approximate form of the structure factor $S(\mathbf{q})$ in the low $\mathbf{q}$ regime.

For a system of rod-like molecules with uniform electron density, the expression for the form factor can be evaluated analytically using a cylindrical coordinate system, as shown in Figure 1 a. For a molecule of length L and radius R, oriented along the direction θ with respect to the nematic director, the form factor is given by

$$f(\mathbf{q}') = \rho \frac{[\exp(iq_z'L) - 1]}{2iq_z'L} \cdot \frac{J_1\left[q_\perp'R\right]}{q_\perp'R}, \quad (5)$$

where $J_1(x)$ is a first order Bessel's function of first kind with argument x. The wavevector, $\mathbf{q}$, in the lab coordinate system and $\mathbf{q}'$ in the molecular coordinate
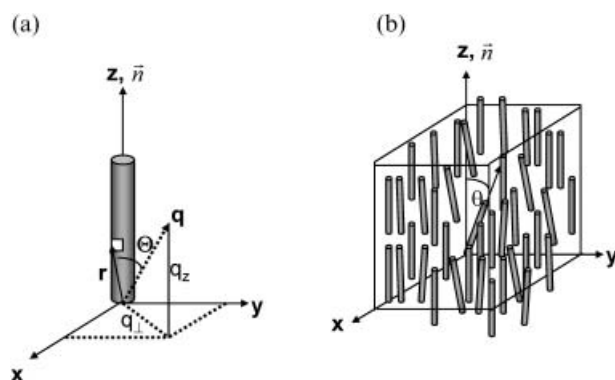

Figure 1. (a) Schematic diagram depicting orientation of the scattering vector and the rod-like LC molecule in the lab frame of reference. (b) The rod-like molecules, on the average, align parallel to the director $\mathbf{n}$. The quality of alignment along $\mathbf{n}$ is determined by the distribution function $f(\theta)$.

system are related to each other through the transformation:

$$q'_x = q_x$$
$$q'_y = q_y \cos\theta + q_z \sin\theta$$
$$q'_z = -q_y \sin\theta + q_z \cos\theta.$$

For a system of rod-like molecules in a nematic phase, where the molecules are aligned on the average parallel to the director **n**, the distribution of the molecules along the director can be approximated by Maier–Saupe like distribution function (8), $f(\theta) = N_\gamma \exp(\gamma \cos^2\theta)$, where N_γ is the normalisation constant such that $\int_0^{\pi/2} \sin\theta d\theta f(\theta) = 1$ and γ is a parameter that determines the strength of the interaction leading to the alignment of molecules. Small value of γ means random alignment of molecules and therefore the isotropic phase. A large value of γ means a preferred alignment of molecules along the director in a nematic phase. The form factor is then given by

$$F(\mathbf{q}) = \int_0^{\pi/2} |f(\mathbf{q})|^2 f(\theta) \sin\theta d\theta. \qquad (6)$$

The form factor, $F(\mathbf{q})$, depends on the distribution of the molecules about the director determined by the distribution function. Figure 2 a depicts the variation of the form factor in two orthogonal directions for rod-like molecules with $L = 27\,\text{Å}$ and $R = 2.5\,\text{Å}$. Although, for a system of randomly distributed rod-like molecules, $\gamma = 0$ [i.e. $f(\theta) = 1$], we used $\gamma = 0.01$ to describe random alignment. For $\gamma = 0.01$, $f(\theta) \sim 1$ and is independent of θ. This allows us to retain the θ dependence in the subsequent integration. When the molecules are randomly aligned ($\gamma = 0.01$) with respect to the director, the form factor plots in q_x–q_z and q_y–q_z planes (upper panels) are identical, i.e. $F(\mathbf{q})$ is spherically symmetric. On the other hand, when the molecules show preferential alignment along the director ($\gamma = 5$), the form factor shows a strongly anisotropic azimuthal distribution. The alignment of the LC molecules has a significant effect on the form factor at both small and large values of q. Additionally, the form factor remains identical in both q_x–q_z and q_y–q_z planes (see Figure 2 a, bottom panel).

Since the form factor and the structure factors are coupled, it is difficult to obtain an analytical expression for the structure factor. However, for rod-like molecules with their long molecular axes aligned along the z-direction, the structure factor for small $\mathbf{q}$ can be approximated by the well known Lorentzian form, often used for the smectic fluctuations. It has been modified to have three different positional order correlation lengths, in the three spatial dimensions as (6):

$$S(\mathbf{q}) \propto \frac{1}{1 + \xi_z^2(q_z - q_0)^2 + \xi_x^2 q_x^2 + \xi_y^2 q_y^2}, \qquad (7)$$

where ξ_i are the correlation lengths along the respective directions and $q_0 = 2\pi/\xi_z$ is the *smectic* wavevector. For simplicity, correlation lengths can be approximated as $\xi_x = \xi_y = 2R$ and $\xi_z = L$. It should be noted that this structure factor assumes a mass density modulation along z direction with correlation length comparable to the nearest neighbour distance, L, as expected of liquids. The observed X-ray scattering intensity is then the product $F(\mathbf{q}) \times S(\mathbf{q})$, averaged over orientations of different domains in the nematic phase, convoluted with the instrumental resolution function. For simplicity, we assume that the system consists of a
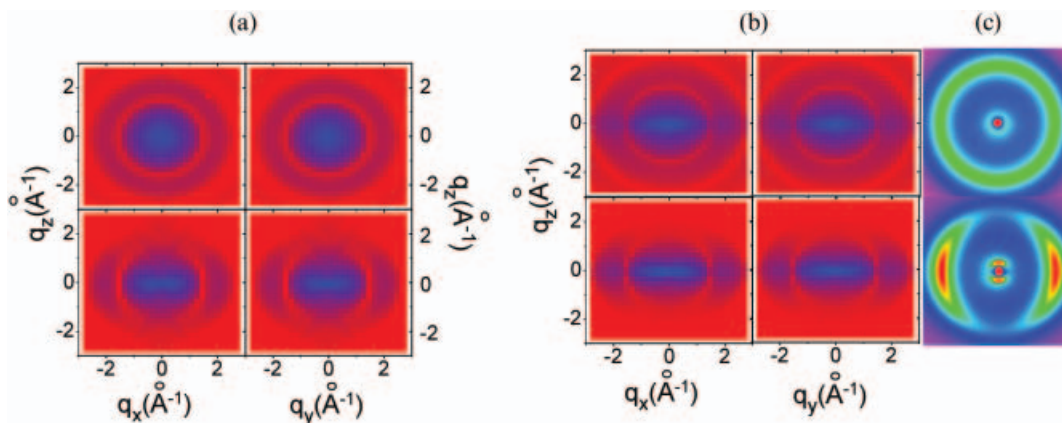

Figure 2. Variation of (a) the form factor, $F(\mathbf{q})$, and (b) X-ray scattering intensity, $I(\mathbf{q})$, on two orthogonal planes in **q**-space. The top panels are for $\gamma = 0.01$ and the bottom two panels are for $\gamma = 5$. The two-dimensional X-ray diffraction pattern intensity from isotropic (top) and nematic phase (bottom) of 5CB are shown in (c).

nematic monodomain and that the instrumental resolution function is infinitely narrow. In that case, the observed intensity in **q**-space is given by $I(\mathbf{q}) = F(\mathbf{q}) \times S(\mathbf{q})$.

Using the above approximations, we have calculated the scattered intensity in two orthogonal planes for the isotropic and nematic phases of the rod-like molecules (Figure 2 b). Evidently, the scattering intensity shows azimuthally symmetric diffuse peaks (Figure 2 b, upper panel), which are the same in the two orthogonal planes, at large angles in the isotropic phase ($\gamma = 0.01$). Since we used a static structure factor with fixed correlation lengths that gives two quasi-Bragg peaks at $q_z = q_0$, there is an anisotropic intensity distribution at the small q-values even for the isotropic phase. For the nematic phase ($\gamma = 5$), the scattered intensity at large **q** becomes anisotropic and strongly concentrated near the x–y plane. At small **q**, the intensity is concentrated on the z-axis in the two diffuse peaks at $q_z = \pm q_0$ along the director. The outer crescents are located perpendicular to the nematic director at the q_x and q_y values corresponding to the diameter of the rods. It should be noted that the diffraction patterns are symmetric with respect to the z-axis and almost identical in the two orthogonal planes and indicating the nematic phase of rod like molecules. These calculated diffraction profiles are in *qualitative* agreement with the experimental diffraction patterns obtained for the isotropic and nematic phases of 4-cyano-4′-pentylbiphenyl (Figure 2 c). This material exhibits a uniaxial nematic phase below the isotropic phase. In order to record these diffraction patterns, the sample was filled in a capillary tube, heated to the isotropic phase and slowly cooled in the presence of an *in-situ* magnetic field of 2.5 kG that aligned the nematic director along the field. The sample was exposed to synchrotron X-ray radiation at 0.765 Å and the scattered intensity was recorded using a two-dimensional area detector.

We also note that the diffraction pattern from the nematic phase *may not* exhibit two diffuse peaks at small angle. It depends on the mosaic distribution of the nematic domains and the phase sequence. For example, the diffraction pattern from a nematic phase with randomly aligned domains is similar to that from an isotropic liquid. In order to distinguish the nematic phase from an isotropic fluid, the director needs to be aligned by first heating the sample to the isotropic phase and slowly cooling to the nematic phase in the presence of an external magnetic (*1*). If the underlying phase is the SmC phase, diffraction pattern close to the N–SmC transition may exhibit four diffuse peaks at small angle due to the pre-transitional thermal fluctuations. This behaviour was mistakenly thought of as a distinct phase and was referred to as the "cybotactic"

nematic phase (*6*). The four peaks persist in the vicinity of the N–SmC transition and the correlation lengths associated with the observed peaks are larger than the molecular dimension. Moreover, the correlations grow with decreasing temperature. These characteristics are absent in the peaks observed by us. However, because of the randomness of the nematic domains (or, correlation volumes), the XRD patterns are identical in two orthogonal planes. Normal laboratory electric fields are unable to overcome the thermal fluctuations and to affect the diffraction patterns.

3.   Diffraction from bent-core molecules

The scattering from molecules depends on their shape and thus the electron density distribution. The form factor for bent-core molecules is clearly different from that for the rod-like molecules. Since a bent-core molecule has two segments joined at an apex, a plane containing the two segments can be defined as the *segment plane*. We approximate the structure of these molecules by two solid cylindrical segments of length L and radius R connected at a fixed apex angle α (see Figure 3 a). While calculating the form factor for such bent-core molecules, one must take into account both the alignment of their long axes and the orientation of the segment planes (or their apex).

We further make a simplifying assumption that the electron density distribution is uniform over the cylindric segment volumes. A lab coordinate system can be defined such that the overall long axis of the bent-core molecule is aligned along the z-axis and the short axis towards the apex (or, the segment plane) of the molecule makes an angle φ with y-axis. In the *segment coordinate system $x'y'z'$* where the long axis of the segment is parallel to the z'-direction, the form factor of the segment of the bent-core molecule is given as:

$$
\begin{aligned}
f_{seg1}(\mathbf{q}') &= \int\limits_{seg1} e^{i\mathbf{q}\cdot\mathbf{r}} d^3 r \\
&= \int_0^L dz \int_0^{2\pi} d\varphi \int_0^R d\rho \rho e^{i(q'_\parallel z + q'_\perp \rho \cos\varphi)} \quad (8) \\
&\propto \frac{e^{iLq'_\parallel} - 1}{iLq'_\parallel} \cdot \frac{J_1(Rq'_\perp)}{Rq'_\perp},
\end{aligned}
$$

where $\mathbf{q}'$ is the reciprocal lattice vector and $J_1(x)$ is a first order Bessel function of first kind with argument x. The form factor for the molecule, in the lab frame, is then given by,

$$
f(\mathbf{q}) = \left| f_{seg1}(\mathbf{q}') + f_{seg2}(\mathbf{q}'') \right|^2, \quad (9)
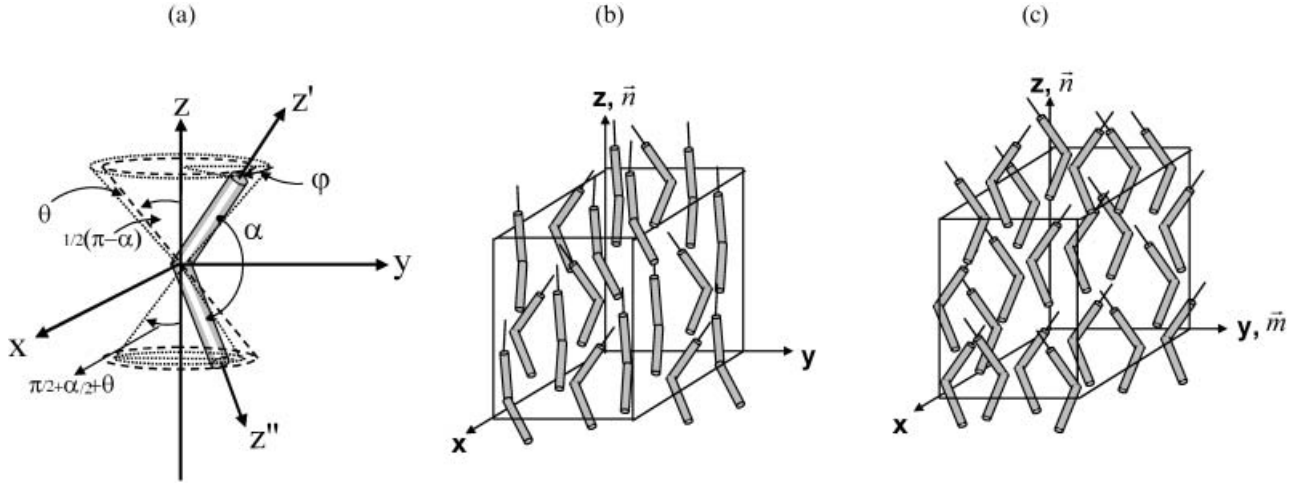$$

Figure 3. (a) Schematic diagram depicting orientation of the bent-core molecule in the lab frame of reference. The form factor of the molecule can be calculated by making the transformation to the segment coordinate system. The molecular organisation of the bent-core molecules exhibiting (b) uniaxial and (c) biaxial nematic phases. The distribution of the molecular long axis and the plane of the bent-core molecules about the semi-major director **n** and semi-minor director **m** is given by the distribution functions $f(\theta)$ and $f(\varphi)$, respectively.

where $\mathbf{q}'$ and $\mathbf{q}''$ are related to $\mathbf{q}$ through the following coordinate transformations:

$$q'_x = q_x[\cos\varphi\cos\psi - \cos(\pi/2 - \alpha/2 + \theta)\sin\varphi\sin\psi]$$
$$+ q_y[\cos\psi\sin\varphi + \cos(\pi/2 - \alpha/2 + \theta)\cos\varphi\sin\psi]$$
$$+ q_z\sin(\pi/2 - \alpha/2 + \theta)\sin\psi$$

$$q'_y = q_x[-\cos(\pi/2 - \alpha/2 + \theta)\cos\psi\sin\varphi - \cos\varphi\sin\psi]$$
$$+ q_y[\cos(\pi/2 - \alpha/2 + \theta)\cos\varphi\cos\psi - \sin\varphi\sin\psi]$$
$$+ q_z\sin(\pi/2 - \alpha/2 + \theta)\cos\psi$$

$$q'_z = q_x\sin(\pi/2 - \alpha/2 + \theta)\sin\varphi$$
$$+ q_y[-\cos\varphi\sin(\pi/2 - \alpha/2 + \theta)]$$
$$+ q_z\cos(\pi/2 - \alpha/2 + \theta)$$

$$q''_x = q_x[\cos\varphi\cos\psi - \cos(\pi/2 + \alpha/2 + \theta)\sin\varphi\sin\psi]$$
$$+ q_y[\cos\psi\sin\varphi + \cos(\pi/2 + \alpha/2 + \theta)\cos\varphi\sin\psi]$$
$$+ q_z\sin(\pi/2 + \alpha/2 + \theta)\sin\psi$$

$$q''_y = q_x[-\cos(\pi/2 + \alpha/2 + \theta)\cos\psi\sin\varphi - \cos\varphi\sin\psi]$$
$$+ q_y[\cos(\pi/2 + \alpha/2 + \theta)\cos\varphi\cos\psi - \sin\varphi\sin\psi]$$
$$+ q_z\sin(\pi/2 + \alpha/2 + \theta)\cos\psi$$

$$q''_z = q_x\sin(\pi/2 + \alpha/2 + \theta)\sin\varphi$$
$$+ q_y[-\cos\varphi\sin(\pi/2 + \alpha/2 + \theta)]$$
$$+ q_z\cos(\pi/2 + \alpha/2 + \theta)$$

where φ, $(\pi/2 - \alpha/2 + \theta)$, ψ and φ, $(\pi/2 - \alpha/2 + \theta)$, ψ are the two sets of Euler's angle for the two different segments of the bent-core molecule. The orientation of a bent-core molecule can be completely defined by

these six angles. Clearly, the form factor depends not only on the angle between the two segments but also on the relative orientation of the segment plane. For simplicity, we assume that the segment plane is always perpendicular to the x–y plane in the lab frame. We allow the molecular long axis and the segment plane to have a finite distribution about the z-axis and y-axis, respectively. Mathematically, this amounts to setting $\psi = 0$.

For a system of bent-core molecules forming a nematic phase, where the molecules are aligned on the average along the major director **n** and the planes of the molecules are aligned along the minor director **m**, the distribution of the molecules can be specified by two angles, θ and φ. We introduce an orientational distribution function, $f(\theta, \varphi)$, with normalisation condition $\int_0^{2\pi} d\varphi \int_0^{\pi/2} \sin\theta d\theta f(\theta, \varphi) = 1$, that describes the orientational distribution of the long axes and segment planes. In terms of the distribution function, the form factor is written as:

$$F(\mathbf{q}) = \int_0^{2\pi} d\varphi \int_0^{\pi/2} |f(\mathbf{q})|^2 f(\theta, \varphi)\sin\theta d\theta. \quad (10)$$

The contribution from the form factor to the scattered intensity at a point in **q**-space depends not only on the internal electron density of individual molecules but also on the orientational distribution of their long molecular axis and the segment plane. The actual distribution of molecular planes depends on factors such as the electrostatic interaction between the molecules, the dimension of the molecule, temperature, etc. For simplicity, we can assume

that the molecular distribution function is separable into two functions, such that $f(\theta, \varphi) = f(\theta) \times f(\varphi)$. We approximate both distribution functions by Maier–Saupe like functions, $f(\theta) = N_\gamma \exp[\gamma \cos^2 \theta]$ and $f(\varphi) = N_\beta \exp[\beta \cos^2 \varphi]$ where $N_{\gamma,\beta}$ are normalisation constants, and γ and β are related to the strengths of the interactions that determine the alignment of molecules along the major and minor directors, respectively. The phase with $\gamma = \beta = 0$, where both the long molecular axes and segment planes are randomly distributed, is the isotropic phase. A phase with $\gamma > 0$ and $\beta = 0$, where the long molecular axis are oriented along **n** and segment planes are randomly distributed, is the uniaxial nematic phase (Figure 3 b). The phase with $\gamma > 0$ and $\beta > 0$ gives rise to alignment of both the long molecular axes and the segment planes along **n** and **m**, respectively. This corresponds to the biaxial nematic phase (Figure 3 c). The uniaxial order parameter then can be defined in terms of the orientational distribution function as $S = \frac{1}{2} \int_0^{\pi/2} \sin \theta d\theta f(\theta) \left[3 \cos^2 \theta - 1 \right]$. For $\psi = 0$, the biaxial order parameter can be written as (*13*):

$$\sigma = \frac{1}{2} \int_0^{\pi/2} \sin \theta d\theta f(\theta) \left[\cos^2 \theta + 1 \right] \int_0^{2\pi} d\varphi f(\varphi) \cos 2\varphi. \quad (11)$$

Using these approximations, we have calculated the form factor contribution to the scattering intensity for a system of bent-core molecules, with $L = 27$ Å, $R = 2.5$ Å and $\alpha = 140°$, in two orthogonal planes for different values of γ and β. For a system with $\gamma = 5$, $\beta = 0.01$, where the long molecular axes are aligned along the director and the segment planes are randomly distributed (the uniaxial phase), the form factor exhibits identical behaviour in two orthogonal planes at both small and large q-values (top panels in Figure 4). However, when the azimuthal symmetry is broken by allowing the segment planes to align along the preferred direction by introducing $\beta = 5$, the form factor shows different behaviour in two orthogonal planes. The XRD pattern at small **q** displays the symmetry of the bent-core molecules, as expected (bottom panels in Figure 4).

The structure factor, or the contribution from the interparticle interference, for the system of bent-core molecules is related to the mass density fluctuations. At small **q**, it can be approximated by a similar mathematical (Lorentzian) expression as used for rod-like systems:

$$S(\mathbf{q}) \propto \frac{1}{1 + \xi_z^2 (q_z - q_0)^2 + \xi_x^2 q_x^2 + \xi_y^2 q_y^2}, \quad (12)$$

where $q_0 = 2\pi/\xi_z$ is the *smectic* wavevector. In contrast to the rod-like molecules where the two correlation lengths perpendicular to the director are identical, the *effective positional* correlation lengths, ξ_i, for the bent-core molecules along three orthogonal directions are now allowed to be different. These correlation lengths in three directions depend on the relative orientation of the molecule. Assuming that all molecules are aligned along the director **n**, the correlation length along this direction reflect the liquid like positional correlations between molecules which should be comparable to the effective molecular dimension along the director. However, the correlation lengths along the two orthogonal directions perpendicular to **n**, depend on the relative orientation of the segment planes. If the segment planes are completely random, as shown in Figure 3 b, the two transverse correlation lengths are equal. On the other hand, if the segment planes exhibit preferential alignment along *y*-axis (Figure 3 c) the two transverse correlation lengths become different but reflect the effective molecular dimensions in the respective directions. For simplicity, correlation lengths can be approximated as,

$$\xi_y = 2L \sin\left(\frac{\pi - \alpha}{2}\right),$$

$$\xi_x = 2R,$$

and

$$\xi_z = 2L \cos\left(\frac{\pi - \alpha}{2}\right).$$

The observed X-ray scattering intensity is then the product $F(\mathbf{q}) \times S(\mathbf{q})$ averaged over different orientations of different domains in the nematic phase convoluted by the instrumental resolution function. Note that, besides imposing a nematic ordering and shape biaxiality, i.e. asymmetry in the correlation lengths along *x*- and *y*-directions, we have not made any explicit assumption regarding the phase biaxiality or the ordering of the segment planes. To simplify things further, let us assume that the system consists of a monodomain nematic phase with all the molecules, on the average, aligned along the *z*-axis and a perfect instrumental resolution. Then the scattered X-ray intensity, $I(\mathbf{q})$, is given by: $I(\mathbf{q}) = F(\mathbf{q}) \times S(\mathbf{q})$.

For a system of bent-core molecules, the scattered intensity at a point in **q**-space depends on the orientational distributions determined by parameters β and γ. Figure 5 shows plots of the intensity $I(\mathbf{q})$ in two orthogonal planes calculated for molecules with $L = 27$ Å, $R = 2.5$ Å and $\alpha = 140°$ for different values of β and γ (i.e. different values of order parameters S and σ). In the isotropic phase ($\beta = 0.01$, $\gamma = 0.01$),
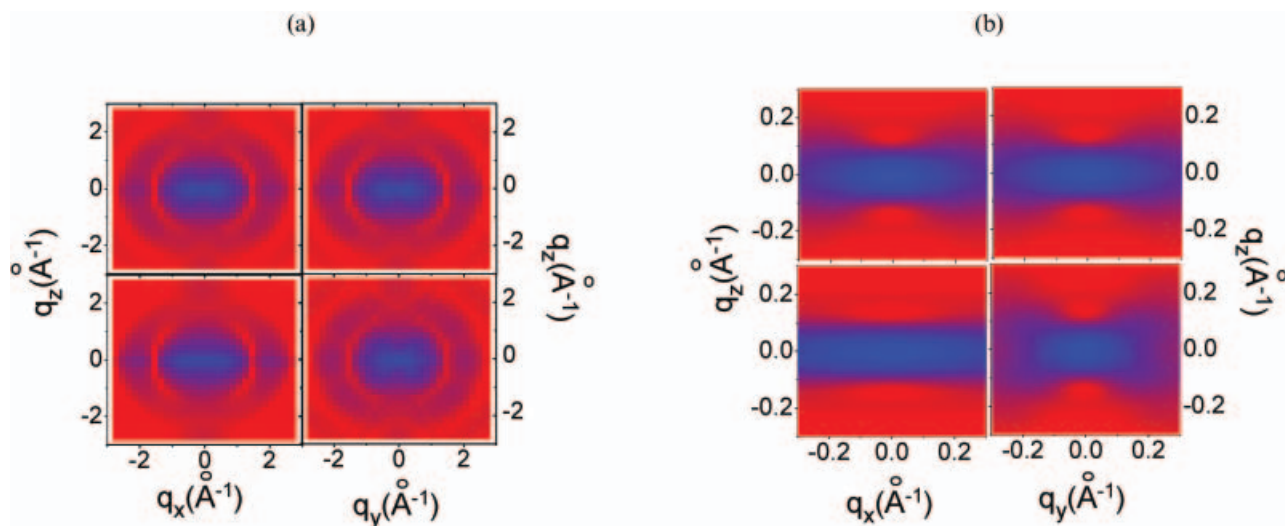
Figure 4. (a) Variation of the form factor, $F(\mathbf{q})$, in two orthogonal planes in $\mathbf{q}$-space for $\gamma=5$, $\beta=0.01$ (top) and $\gamma=5$, $\beta=5$ (bottom). Although the outer diffuse rings appear identical on both planes the form factor at small $\mathbf{q}$ exhibit different behaviour, as shown in (b).

where all molecules are randomly distributed in space, the scattered intensity distributions in both planes are identical. As expected for an isotropic liquid, the scattered intensity at large $\mathbf{q}$ is azimuthally isotropic in both planes (top panels in Figure 5 a). Since we have used a static structure factor that gives two diffuse peaks at $q_z=q_0$ (the peaks lie on the z-axis and are azimuthally symmetric), two diffuse peaks appear instead of a diffused ring at small $\mathbf{q}$ (top panels, Figure 5 b).

Depending upon the nature of interactions among the bent-core molecules, two different nematic phases are possible. The uniaxial nematic phase results when the segment planes are randomly distributed around the z-axis, i.e. the director for $\gamma>0$ and $\beta=0$. Since the two directions orthogonal to $\mathbf{n}$ are degenerate, the diffraction patterns in these two directions are identical. The diffraction patterns reflect the symmetry of the molecules and consist of four diffuse peaks at small $\mathbf{q}$ instead of the two as for
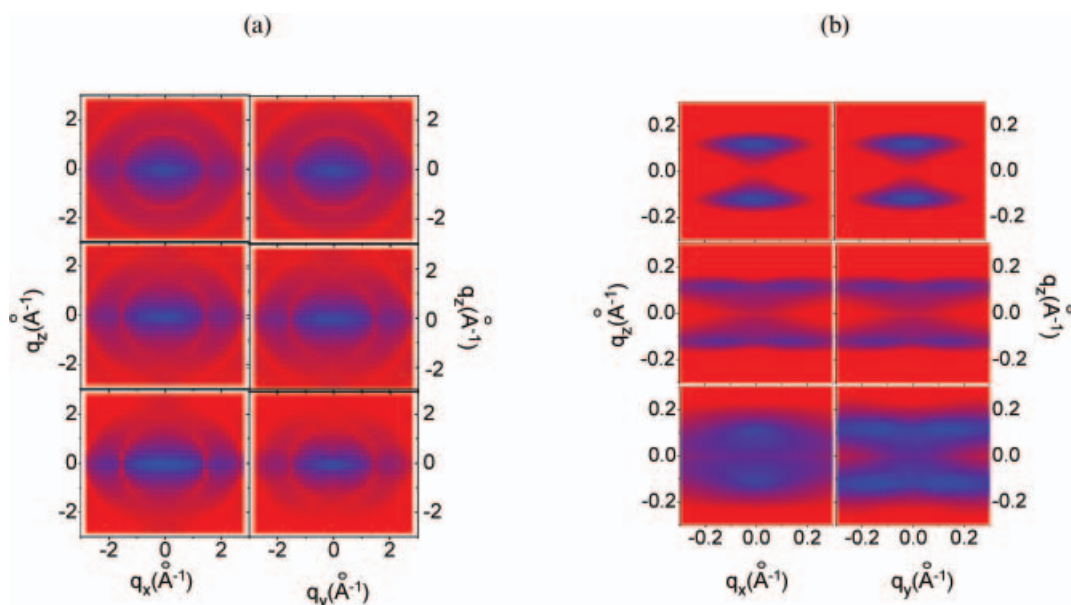

Figure 5. (a) Variation of the scattered intensity, $I(\mathbf{q})$, in two orthogonal planes in $\mathbf{q}$-space for $\gamma=\beta=0.01$ (top) $\gamma=5$, $\beta=0.01$ (middle), and $\gamma=\beta=5$ (bottom) at small angle. (b) The scattered intensity at the small $\mathbf{q}$-values. For $\gamma=\beta=5$, unequal correlation lengths were used in two different directions to incorporate the effect of the molecular distributions.

rod like molecules. At large angles, the XRD pattern from the biaxial nematic phase consists of two lateral diffuse peaks arising from the alignment of the long molecular axes. Most importantly, the diffraction patterns at small angle depend on the orientation of the segment planes with respect to the incident X-ray beam. When the beam is incident perpendicularly to the segment planes, the diffraction pattern consists of four diffuse peaks. However, when the X-ray beam is incident parallel to the segment plane, only two peaks are observed. The middle panels in Figure 5 a depict the calculated diffraction patterns in the two orthogonal planes for a system of bent-core molecules having near perfect alignment of the long molecular axis ($\gamma=5$) and almost random alignment of the segment planes ($\beta=0.01$). The bottom panels, on the other hand, shows the pattern for the case where, both, the long molecular axes and the segment planes are highly aligned ($\gamma=5$ and $\beta=5$) along their respective directors. Corresponding enlarged view of the small angle diffraction pattern are shown in Figure 5 b. The presence of four diffuse peaks at small **q** in two the orthogonal planes containing the director confirms the uniaxial nematic phase. However, if the diffraction pattern in the two orthogonal planes consists of two distinct patterns (two diffuse peaks in one plane and four diffuse peaks in the other) it provides the evidence for the biaxial nematic phase.

The XRD pattern from the uniaxial nematic phase composed of bent-core molecules will have four diffuse peaks in the two orthogonal orientations with respect to the incident X-ray beam, i.e. with the beam parallel/perpendicular to the segment plane. Here, we note that the mere existence of four diffuse peaks is not an indication of the biaxial nematic phase. The four peaks merely reflect the symmetry of the molecules. A fully developed and aligned biaxial nematic phase will have four diffuse peaks with the X-ray beam incident perpendicular to the plane containing the segment planes and only two diffuse peaks in the orthogonal direction. If the system enters to the biaxial nematic phase from the uniaxial nematic phase and the second director is well aligned, the four diffuse peaks in one of the planes will remain unchanged and the four diffuse peaks in the other planes gradually merge into two.

In order to realise these changes in experiments, LC cells are fabricated using two polished beryllium substrates coated with polyimide films (*10*). The polyimide films are unidirectionally rubbed and put together in antiparallel manner, with $\sim 50\,\mu m$ gap and filled with the LC. Any phase transition affected by the surface ordering at the substrate–LC interface will permeate entire cell only when the coherence length ($\sim 1\,\mu m$) associated with the surface energy (*14*) is comparable to the cell gap. Clearly, the experimental cells allow the alignment of primary director throughout the cell, they behave as a bulk sample, and therefore the surface induced biaxiality is not a concern. The coupling strength between the applied electric field and the dielectric anisotropy of the molecules is insufficient to overcome thermal effects and impose an orientational ordering and change the diffraction pattern.

Next, let us consider the case when the nematic phase develops from the isotropic phase such that the long molecular axis and the segment planes gradually align in the respective directions, **n** and **m**. At a temperature close to the transition, both the uniaxial and biaxial order parameters are small. As a consequence, there are two identical pairs of diffused peaks in two orthogonal directions. The system effectively appears as a uniaxial phase of a rod-like system. As the temperature is further lowered, both uniaxial and biaxial nematic orders gradually increase. At sufficiently low temperature, the diffraction patterns in the plane parallel to the segment planes gradually splits into four diffused peaks. However, the two diffuse peaks in the transverse direction remain unchanged except for quantitative changes in the scattered intensity. Appearance of distinct diffraction patterns in two orthogonal planes is an indication of the biaxial nematic phase.

The detail interaction between the bent-core molecules determines the phase sequence and therefore the nature of the XRD pattern. If intermolecular interactions favour the alignment of the long molecular axes prior to the alignment of the segment planes, the diffraction pattern displaying four diffuse peaks in a plane perpendicular to the segment planes will remain but the four diffuse peaks in the orthogonal plane gradually merge into two in a well aligned biaxial nematic phase. If the interaction, on the other hand, favours the simultaneous alignment of the long molecular axes and segment planes, the diffraction ring observed with the incident beam perpendicular to the segment planes will gradually transform into four diffuse peaks. In the orthogonal direction, the ring will condense into two diffuse peaks. A recently reported (*15*) second-order phase transition from the uniaxial to biaxial nematic phase in azo-substituted bent-core molecules is in agreement with this prediction. Figure 6 shows evolution of the diffraction pattern in a sample of bent-core molecules as the temperature is lowered and the order parameters grow. The qualitative agreement between the theoretical prediction and the experimental diffraction pattern in these molecules suggests that, both, the molecular axes and the segment

planes simultaneously align along their respective directions. Near the nematic–isotropic transition, the ordering of the long molecular axis (or **n**) is higher than for the segment planes, and therefore the system behaves as a uniaxial nematic. As the nematic phase further develops at lower temperature the ordering of the segment planes also becomes significant and the system behaves as a biaxial nematic. We also note that with the inclusion of a temperature dependent parameter to account for changes in intensity as a function of temperature, it should be possible to obtain the distribution functions and the order parameters using the observed diffraction patterns. A theoretical model incorporating the temperature dependence of diffraction pattern and calculations of the order parameters will be reported elsewhere.

4.   Conclusions

Using the simple form factor, we have calculated diffraction patterns for a system of rod like molecules. With a simple Maier–Saupe like orientational distribution function for the single particle distribution,

we demonstrate that the calculated diffraction patterns are in excellent agreement with the experimental data. The same model has been extended to calculate the diffraction pattern for a system of bent-core molecules. Two different distribution functions were used for the alignment of their long molecular axes and the segment planes. The results show that depending upon the nature of interaction, the aggregate of the bent-core molecules exhibit only four diffuse peaks or two and four diffuse peak in two orthogonal planes in the uniaxial or biaxial phases, respectively. In the uniaxial nematic phase, the diffraction patterns exhibit four diffuse peaks in two orthogonal planes containing the director **n**. The biaxial nematic phase, on the other hand, exhibits diffraction patterns comprised of four diffused peaks in one plane and two diffuse peaks in the orthogonal direction. Governed by the nature of intermolecular interactions, a system may exhibit a uniaxial nematic phase below the isotropic phase or it might directly enter the biaxial nematic phase. We also note that using simple theoretical models, the azimuthal distribution of XRD intensity can be used to estimate the distribution function and therefore the order parameter in, both, the uniaxial and the biaxial
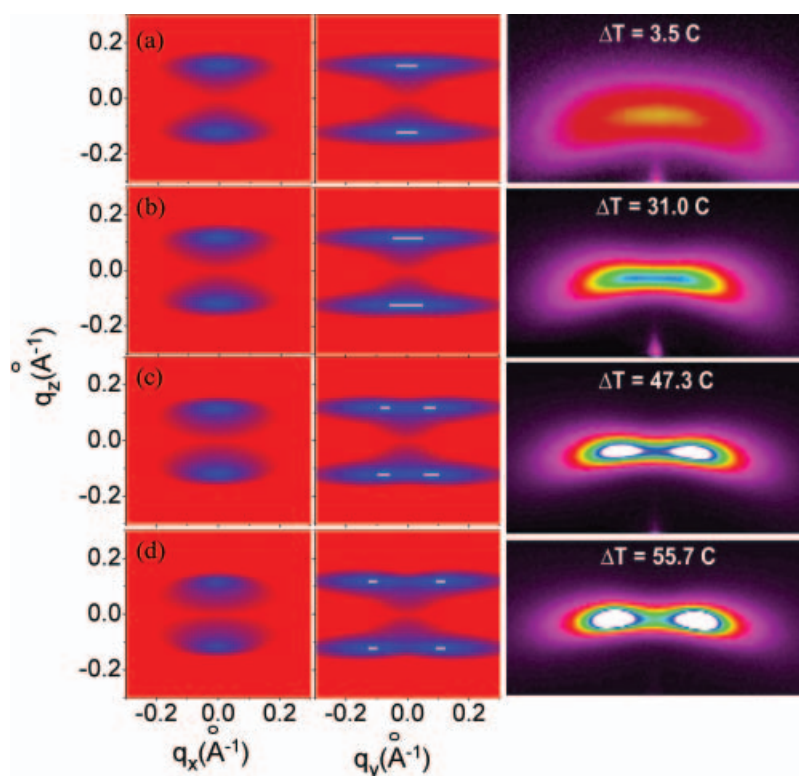

Figure 6. Variation of the scattered intensity, $I(\mathbf{q})$, in two orthogonal planes in **q**-space for (a) $\gamma=\beta=1$, (b) $\gamma=\beta=2$, (c) $\gamma=\beta=3$ and (d) $\gamma=\beta=4$. The left and right columns depict the scattered intensity in q_x–q_z and q_y–q_z planes, respectively. For these calculations, owing to the shape biaxiality of the molecules unequal correlations lengths along two different directions perpendicular to the major director were used. These correlation lengths were calculated as described in the text. The panels on the right show observed scattered intensity at different reduced temperatures as the sample in a capillary tube is cooled to the nematic phase from the isotropic phase.

nematic phases. Therefore, the XRD experiment not only provides a qualitative identification of the biaxial nematic LC phase but also has the potential to allow quantitative determination of the two order parameters.

Acknowledgments

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