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Translational and orientational order parameters of the 3,5-bis-(p-5-hexenyl-1-oxyphenyl)-isoxazole by X-ray diffraction

Z. X. Fan^a; C. G. Seguel^b; C. Aguilera^b; W. Haase^a

^a Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Darmstadt, Germany ^b

Departamento de Química, Facultad de Ciencias, Universidad de Concepcion, Chile

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**Translational and orientational order parameters
of the 3,5-bis-(p-5-hexenyl-1-oxyphenyl)-isoxazole
by X-ray diffraction**

by Z. X. FAN†, C. G. SEGUEL‡, C. AGUILERA‡ and W. HAASE†*

† Institut für Physikalische Chemie, Technische Hochschule Darmstadt,
Petersenstraße 20, D-6100 Darmstadt, Germany

‡ Departamento de Química, Facultad de Ciencias,
Universidad de Concepcion, Chile

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A new liquid crystal compound 3,5-bis-(p-5-hexenyl-1-oxyphenyl)-isoxazole has been characterized using X-ray diffraction. From the detailed study of the inner and outer reflection, along the meridional and equatorial directions, respectively, the orientational and translational order parameters have been determined in the nematic and smectic A phases.

1. Introduction

Knowledge about the structure of the liquid crystal phases is mainly acquired by diffraction measurements [1, 2]. The structures can be classified as one, two and three dimensionally partially ordered systems. The structure of the S_A phase is usually represented on the assumption of the presence of an almost pure sinusoidal density wave, because in conventional medium measurements they are indistinguishable from the ordinary Bragg reflections. However, very high resolution X-ray diffraction measurements show that the diffraction pattern is not composed of infinitely sharp delta function peaks [3]. Therefore, Leadbetter has pointed out that the usual depiction of the S_A phase as well defined, sharp layers is very misleading [4]. Taking into account the fluctuation of S_A layers, one fan shaped scattering model has recently been suggested to describe the scattering phenomenon of the oriented S_A structure [5, 6]. Here this method is used to determine the translational order parameter for one low molecular liquid crystal compound from the X-ray measurements. The orientational order parameter and the packing in the smectic A and nematic phases are also discussed.

2. Theoretical background

To identify the different liquid-crystalline phases the essential features of the structural order can be extracted in terms of a few simple parameters, e.g. the macroscopic orientational state can be described using the orientational order parameter. For a uniaxial oriented phase the X-ray diffraction patterns in the θ - ϕ plane [7, 8] reflects the orientational state so that the molecular orientational distribution function $f(\beta)$ can be calculated from the X-ray equatorial outer reflection. A

* Author for correspondence.

relationship between the integral intensity $I(\phi)$ around the diffuse equatorial arc and $f'(\beta)$ is [8, appendix A]

$$I(\phi) = \int_{\beta=\phi}^{\pi/2} f'(\beta) (\sin^2 \beta - \sin^2 \phi) \sec \phi \, d\beta, \tag{1}$$

and the orientational order parameters $\langle P_L \rangle$ can be estimated from $f(\beta)$

$$\langle P_L \rangle = \frac{\int_0^{\pi/2} P_L(\cos \beta) f(\beta) \sin \beta \, d\beta}{\int_0^{\pi/2} f(\beta) \, d\beta}, \tag{2}$$

where $P_L(\cos \beta)$ is the L th rank Legendre polynomial with $L=2, 4, \dots$

The uniaxially oriented S_A phase shows a two dimensional fluctuated layer structure. Its translational order can be quantified by means of the translational order parameter τ . This can be considered as the normalized correlation length $G(r)$ in a zero-one space, in other words, with two boundary values zero and one. To obtain τ from the X-ray measurements, the key point is to establish the appropriate scattering model. The second is how to combine the experimental data with theory.

In considering the fluctuation of the smectic layers caused by splay deformations, which results in the deviation of the normal vector of the smectic layers from the director direction, fan shaped scattering model has been suggested recently (see figure 1), in which the amplitude of the elastic scattering $f(q)$ of the inner reflection by the field $\sigma(r)$ is defined by [5]

$$f(q) = \int_0^\infty \sigma(r) F(qr, \alpha) r \, dr. \tag{3}$$

Here q is the scattering vector, r is the scattering distance and α is the angular dimension of the curved layers in the S_A phase. In the nematic phase, α should reflect the molecular orientational distribution. It can be determined from the orientational order parameter indirectly. With the simplified assumption that there is a linear distribution of the smectic layers the integral structure factor F referencing the angle extending from $-a$ to $+a$ can be expressed as [6, appendix]

$$F(qr, \alpha) = \int_{-a}^{+a} \exp(iqr \cos \alpha) \, d\alpha \tag{4}$$

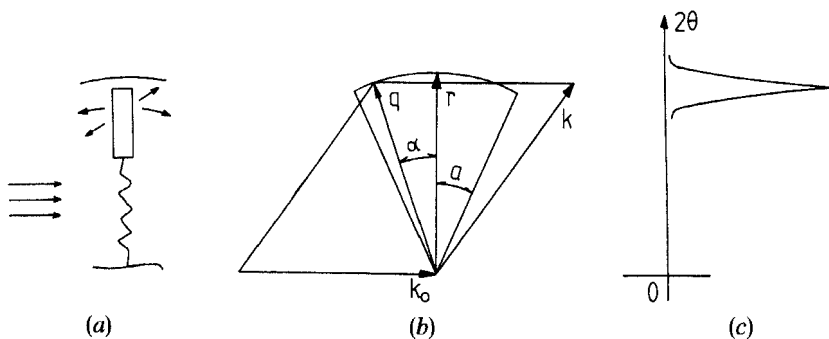


Figure 1. (a) Fan-shaped scattering front of the S_A structure, (b) the scattering vectors, (c) scattering in reciprocal space.

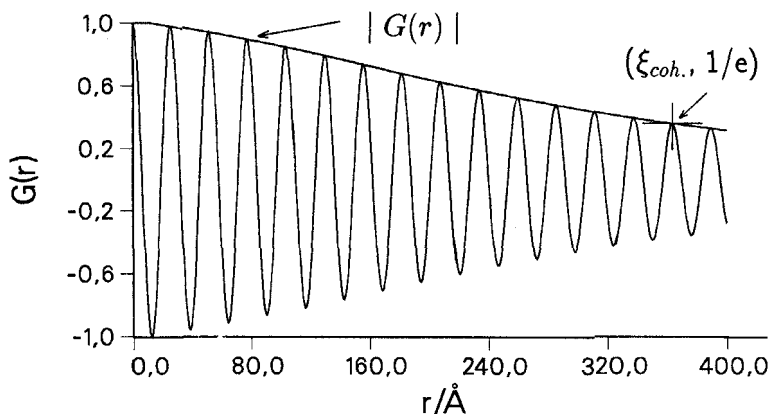


Figure 2. Example of the extraction of the correlation length ξ_{coh} from the correlation function $G(r)$ for the compound investigated at 109.5°C .

$$F(qr, \alpha) = 2\alpha J_0(qr) + \sum_{n=1}^{\infty} (-1)^n \frac{4 \sin(2na)}{n\pi} \int_0^{\pi/2} \cos(qr \sin \theta) \cos(n\theta) d\theta \\ + \sum_{n=0}^{\infty} (-1)^n \frac{8 \sin[(2n+1)a]}{(2n+1)\pi} \int_0^{\pi/2} \sin(qr \sin \theta) \sin(n\theta) d\theta. \quad (5)$$

After the Hankel transform and the convolution calculation on the function $\sigma(r)$ the correlation function $G(r)$ is given by [5, 9]

$$G(r) = H^{-1}[f(q)f^*(q)] = \sigma(r) * \sigma(-r) = \int_{-\infty}^{\infty} \sigma(u)\sigma(u+r) du, \quad (6)$$

$$= \int_{-\infty}^{+\infty} \left\{ \int_0^{\infty} \sqrt{[I(q)]F(qu, \alpha)} dq \int_0^{\infty} \sqrt{[I(q)]F[q(u+r), \alpha]} dq \right\} du, \quad (7)$$

in which $I(q)$ is the normalized two dimensional diffraction profile related to the director direction. $G(r)$ is analogous to the Patterson function; it satisfies $G(0) = 1$ and $G(\infty) = 0$. The detailed process of the data handling of $I(q)$ is described in [6]. From $G(r)$, the coherence length ξ_{coh} , can be extracted as shown in figure 2

$$\xi_{\text{coh}} = \xi_{|G(r)| = 1/e}. \quad (8)$$

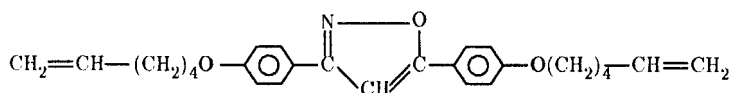
So we can call $|G(r)|$ the extracted correlation function (see figure 2). For the weakly ordered nematic, smectic A and smectic C phase, because there is not a fixed positional order within the layers and between the neighbouring layers, the exponential form can be used to express the translational order parameter τ [6]

$$\tau = \exp\left(\frac{-d_L}{\xi_{\text{coh}} - d_L}\right). \quad (9)$$

In this equation, d_L is the thickness of the smectic layer. ξ_{coh}/d_L can be understood as the average number of the correlated S_A layers. The boundary values of τ are one or zero corresponding to the extreme cases of $\xi_{\text{coh}} = \infty$ and $\xi_{\text{coh}} = d$, respectively.

3. Experimental

The compound 3,5-bis-(p-5-hexenyl-1-oxyphenyl)-isoxazole



was synthesized by means of a cyclization reaction of the respective 1,3-dicarbonyl derived with hydroxylamine; the chemical structure was characterized by IR, ^1H NMR (300 Hz) and ^{13}C NMR (60 MHz) [10]. The thermal behaviour was studied by microscopic observation using a polarizing microscope (Leitz Ortho Plan, POL BK II), equipped with a hot stage (Mettler FP82), and by DSC measurement using a differential scanning calorimeter (Du Pont 990). The S_A -N phase transition was also confirmed by X-ray measurement. Its transition temperature and the transition enthalpies are

$$C \xrightarrow[20.17 \text{ kJ mol}^{-1}]{99.1^\circ\text{C}} S_A \xrightarrow[0.32 \text{ kJ mol}^{-1}]{114.1^\circ\text{C}} N \xrightarrow[1.0 \text{ kJ mol}^{-1}]{144.0^\circ\text{C}} I$$

Before the X-ray measurements, the sample was heated to 143°C and kept for a period of 60 min in an oven equipped with CoSm5 permanent magnets, which produce a magnetic field of about 0.8 T to keep the alignment of the sample during the measurements. After the orientation the sample was cooled slowly (10 K h^{-1}) to the desired temperature and kept for over 30 min. The X-ray measurements are performed with a focusing horizontal two circle X-ray diffractometer (STOE STADI 2). The X-ray source was a long, fine focus X-ray tube SIEMENS FK with a line focus of $0.4 \times 12 \text{ mm}^2$. The Cu- $K_{\alpha 1}$ radiation ($\lambda = 1.54056 \text{ \AA}$) was focused with a curved Ge(111) monochromator. The mechanical and electrical controlled smallest stepwidth of the diffractometer in θ and ω circle is 0.001° . For fast diffractometry, a linear position sensitive detector (STOE Mini PSD) was used with a resolution of the stepwidth 0.01° in the 2θ circle. A detailed description of the X-ray set-up is given in [11].

The orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ were determined from the equatorial outer reflection. The structure of the computer program used has been described elsewhere [5, 8]. For the inner reflection in the meridional direction the diffraction profiles in the Φ - q plane were fitted to second order of the Lorentz function using the STOE-PACKAGE computer program [6, 12]. The full width at half maximum (FWHM) obtained from the fitting calculation were corrected using $\text{FWHM} = \text{FWHM}' - 0.040 - 1.3 \sin(2\theta_0) \times 360 / (220 \times 2\pi)$ because the original widths of the X-ray beam is 0.040° and the thickness of the sample amounts to 1.3 mm. The correlation length and translational order parameter were calculated using the method described in [6].

4. Discussion

As an example, figure 3 shows the inner reflections for the sample at 109.5°C . It shows that the scattering intensities decrease with the increasing angle. In contrast to liquid-crystalline side chain polymers [6], the peak position and the width remain almost unchanged. It means that the S_A phase almost possesses a circle-shaped layer-front structure as represented in figure 1. Figure 4 gives the average value of d and the

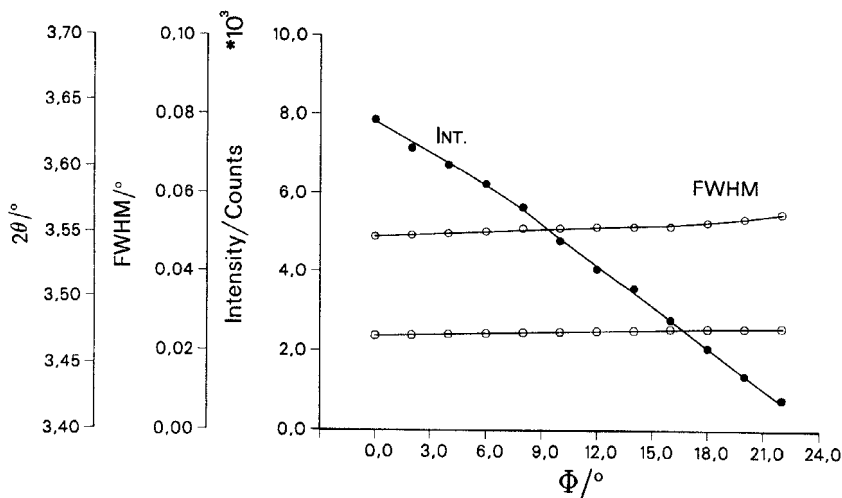


Figure 3. Peak position, maximum intensity and full width at half maximum of the inner reflections at 109.5°C.

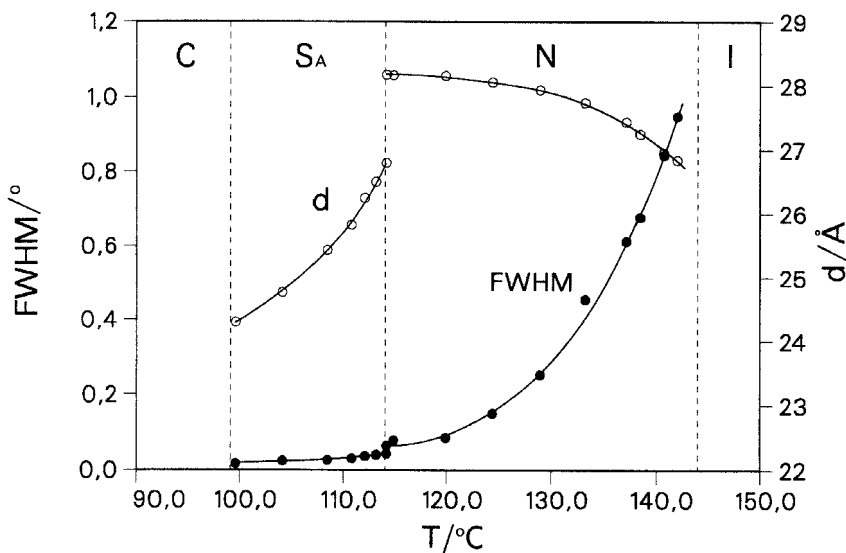


Figure 4. The average d value and the width of the inner reflection versus temperature.

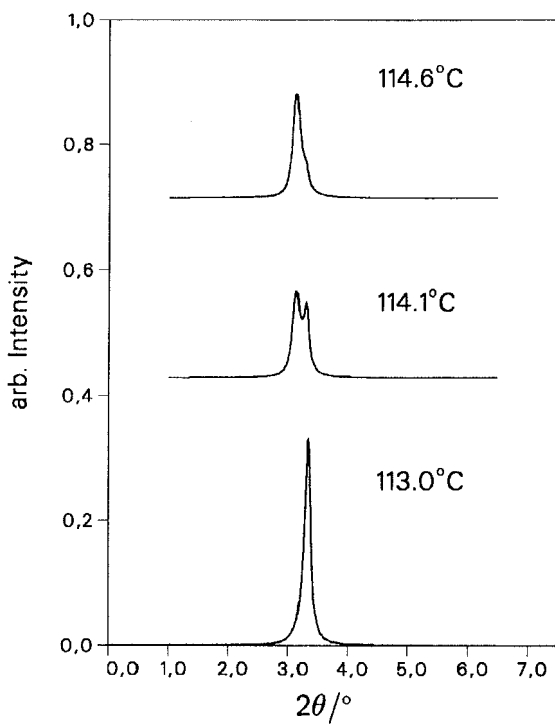


Figure 5. The (001) peaks around the S_A -N transition.

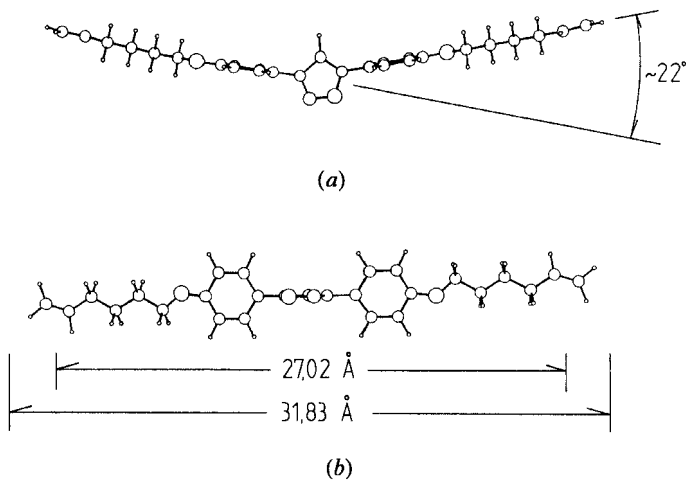


Figure 6. Molecular configuration calculated using the MNDO program, viewed from two orthogonal directions.

width at different temperatures. It shows the width increases discontinuously during the S_A -N phase transition. This can be clearly observed through the change of the (001) peaks around the phase transition in figure 5.

To discuss the molecular packing in a liquid crystal phase, the molecular configuration is simulated using a MNDO program [13]. As shown in figure 6(b), the average molecular length between the four atoms, attached to the end of the C=C double bonds and including the van der Waal's radius, amounts to 31.83 Å. It is larger than the thickness of the S_A phase (24–27 Å). But the average distance between the two C=C end groups is just 27.02 Å. This implies maybe the smectic layers are formed through the overlapping of the terminal C=C bonds as supposed in figure 7. One interesting question is why the smectic thickness decreases with decreasing temperature in the S_A phase and how the molecules aggregate together in the S_A phase. One possibility is that on lowering the temperature the molecular motion in the smectic

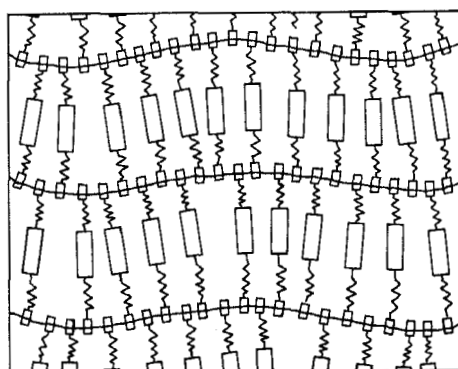


Figure 7. The schematic diagram of the smectic interface with the overlapping of the terminal C=C bonds shown as □-.

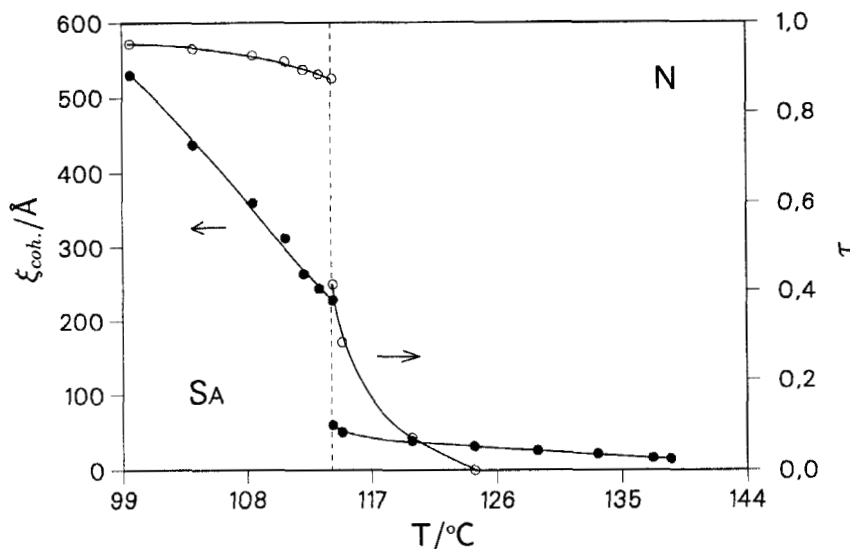


Figure 8. The correlation length and translational order parameter in the S_A and nematic phases.

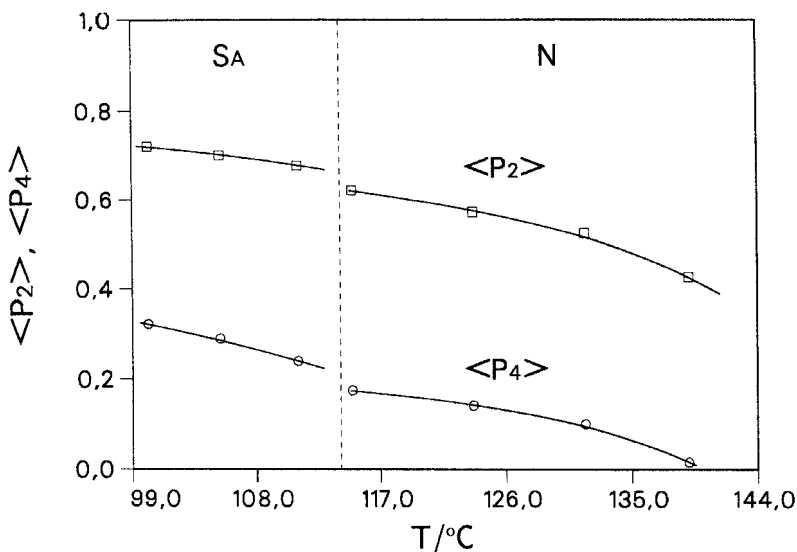


Figure 9. The orientational order parameters calculated from the outer reflection.

layers decreases gradually and the mutual effect between the terminal C=C groups becomes incrementally stronger. Both effects result in the shortening of the S_A layers.

In figure 2, one example to determine the correlation length ξ_{coh} from the correlation function $G(r)$ is displayed. Looking at the profile of the correlation length and the translational order parameter in figure 8, a first order S_A —N phase transition is observed. It was also confirmed by the DSC measurements and the curving tendency of the orientational order parameter (see figure 9). Figure 6(a) shows the bent configuration of the molecule; the geometrical angle between the two wings is roughly 20° . Because the wide-angle scattering of the equatorial arc can be imagined as characteristic of single molecules [14], the molecular structure in figure 6 shows why the orientational order parameter is not high. Besides this, figure 8 shows that the correlation length ξ_{coh} in the nematic phase, especially near the S_A phase, is longer than the molecular length. It confirms the assumption that in the nematic phase there are small S_A -like regions caused by the local fluctuation. This idea has been expressed by Leadbetter [4]. It is also the reason why the inner X-ray peaks in the nematic phase are relatively sharp, especially near the S_A phase.

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