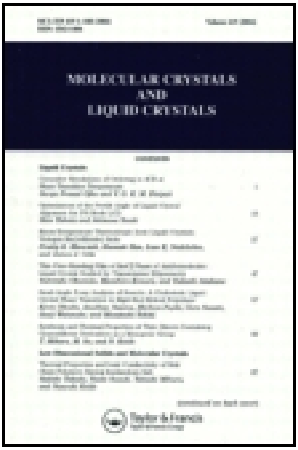

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RAMAN STUDIES OF ORIENTATIONAL ORDERING IN A RE-ENTRANT NEMATIC MIXTURE 8OCB-6OCB

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Raman Studies of Orientational Ordering in a Re-Entrant Nematic Mixture 8OCB-6OCB

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We present the results of our investigations of polarized Raman scattering spectra of the 25% mixture of 6OCB in 8OCB in mesomorphic state, which was studied with the main aim to get deeper insight into specifics of molecular orientational ordering of this substance in various mesophases. Temperature and pressure dependence of $\langle P_2 \rangle$, $\langle P_4 \rangle$ is investigated and compared with the meanfield model.

Keywords: Raman scattering; liquid crystals; re-entrant mesophase

INTRODUCTION

Since first observation of the phase sequence nematic - smectic - re-entrant nematic [1] re-entrant behaviour attains permanent attention of the experimentalists and theoreticians [2-4]. Although these studies explained many features of the re-entrant mesophases (including variation of the smectogenic part of the liquid crystal potential parameters implied, for example, by the model model developed in [5]) they are still far from underrstanding the phenomenon. To analyse the models very often orientational order parameters are required. In this work we perform detailed study of the orientational ordering of the molecules in a classic representative of the re-entrant mesogens: mixture

6OCB-8OCB. We use Raman depolarization measurements for this to get reliable values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$.

BACKGROUND

Order parameters are determined from Raman scattering by measuring integral intensity I_{ij} of a Raman band belonging to some intramolecular mode for various orientations j,i of the polarization of the exciting and the scattered light, respectively[6].For example, for a symmetric intramolecular mode in a uniaxial medium consisting of axially symmetric molecules one can write:

$$r_1 = \frac{I_{xz}}{I_{zz}} = \frac{3a^2\left(7+5\langle P_2\rangle - 12\langle P_4\rangle\right)}{70+140\sqrt{2}a\langle P_2\rangle + 4a^2\left(7+10\langle P_2\rangle + 18\langle P_4\rangle\right)} \qquad (1)$$

$$r_2 = \frac{I_{zx}}{I_{xx}} = \frac{3a^2\left(7+5\langle P_2\rangle - 12\langle P_4\rangle\right)}{70-70\sqrt{2}a\langle P_2\rangle + a^2\left(28-20\langle P_2\rangle + 27\langle P_4\rangle\right)} \qquad (2)$$

where $a=(\partial\alpha_{20}/\partial Q)/\ (\partial\alpha_{00}/\partial Q)$ is dimensionless ratio of the 2 components of the molecular polarizability derivative tensor for a particular intramolecular mode in a cyclic basis set [7], which are related to the Cartesian components by the formulae

$$\alpha_{00} = -(\alpha_{kk}+\alpha_{mm}+\alpha_{nn})/\sqrt{3}, \quad \alpha_{20}=(\alpha_{kk}+\alpha_{mm}-2\,\alpha_{nn})/\sqrt{6},$$

where k, m, n denote principal axes of the molecular fixed system. X, y, z in equations (1)-(2)are the axes of the laboratory system with z being the symmetry axis of the mesophase (similarly to previously introduced definitions[6]). Coefficient a is usually determined from the isotropic phase measurements and, consequently, using (1)-(2) one can investigate $\langle P_2 \rangle$ and $\langle P_4 \rangle$ in the mesophase.

Studies of more general cases of orientational ordering and intramolecular modes, as well as mathematical formalism and experimental methods, such as scattering geometry and correction factors for accompanying phenomena were developed and thoroughly analysed elsewhere[6] and we refer the reader to that paper for detailed explanations.

Experimentally measured Raman depolarization ratios, before being used for determining the order parameters with equations (1)-(2), are subject to recalculations [6, 8]:

$$R_1 = C_n \frac{f_{xx}^2}{f_{zz}^2} r_1 , \quad R_2 = \frac{1}{C_n} \frac{f_{zz}^2}{f_{xx}^2} r_2 , \qquad (3)$$

where $C_n = \frac{(n_g + n_z)^2}{(n_g + n_x)^2}$

is the Lax-Nelson correction factor for distortion of the scattering angle in an anisotropic medium (n_x, n_z are the refractive indices of the liquid crystal and n_g is that of the glass of the cell) and f_{ii} is the local field factor, accounting for the anisotropy of the electric field acting on a molecule in an anisotropic medium, when isotropic external field is applied to it.

EXPERIMENTAL

The mixture of two cyano derivatives 8OCB and 6OCB has been chosen for our studies. Structural formulas of the components and the phase transition temperatures of the mixture at normal pressure are shown below:

C_6H_{13}-O-Ph-Ph-CN	25.1 wt.%
C_8H_{17}-O-Ph-Ph-CN	74.9 wt.%

Cr 20°C N_r 25.7°C SmA 46.8°C N 77.8°C I

These transition temperatures (determined to the accuracy ±0.2°C except crystallization) as well as those under pressure coincide reasonably well with the data presented in [9] where its phase diagram has been studied in more details.

The light scattering spectra in the back scattering geometry were registered by Spex-Ramalog spectrometer model 14018. Raman scattering was excited with the Argon-ion laser lines 514 and 497 nm, with 15-50 mW power incident on the sample. Further spectroscopic details of the experimental arrangement used for the measurements under elevated temperature and pressure as well as the methods for liquid crystal alignment and measuring Raman intensities can be found in [10,11]. Two Raman lines at 2226 cm^{-1} and 1604 cm^{-1} belonging to the cyano stretching and benzene fragment total symmetric intramolecular modes were studied. Depolarization measurements were done as a function of temperature at normal pressure and at 40Mpa and the results are presented in Figure 1. Temperature was controlled within was ±0.1°C. The accuracy of the pressure stabilization was better than ±0.2 MPa. The scattering of the experimental point shows reproducibility of Raman depolarization measurements (it has been noticed that simultaneous registration of all polarization components at every wavenumber, as is described elsewhere[12], substantially increases the signal-to-noise ratio). The influence of systematic errors on polarization measurements was checked by repeated measurements of similar Raman polarized components with different orientation of the cell relative to the spectrometer gratings and polarizers.

Refractive indices of the mixture (which were necessary for the order parameters calculations) in all thermodynamic states of interest were determined by interferometric measurements in polarized light. The correction factor for distortion of the scattering angle in an anisotropic medium determined this way had minor effect on the depolarization ratios (it changed depolarization ratios R_i by about 10-15%).

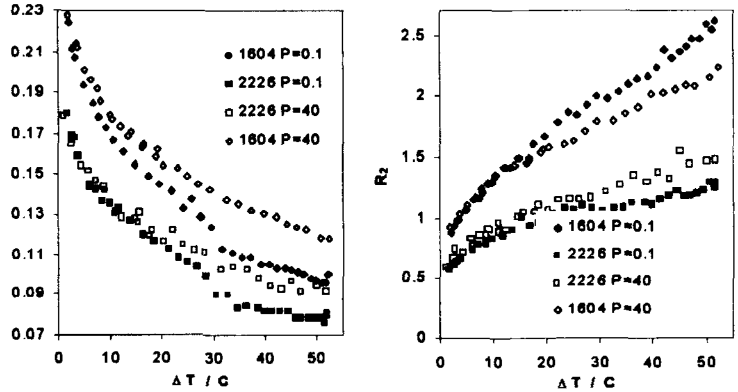

FIGURE 1 Raman depolarisation ratios of the mixture 6OCB-8OCB as a function of temperature for two different pressure values. In the isotropic phase R_{2226}= 0.265, R_{1604}= 0.377. $\Delta T=T_{NI}-T$. At P=0.1 MPa T_{NI}=77.8°C; at P=40 MPa T_{NI}=92°C.

RESULTS AND DISCUSSION

Several models were proposed to determine anisotropy of the Lorentz tensor L to perform local field correction in equation (3) using definition

$$f_{ii} = 1 + L_{ii}\left(n_i^2 - 1\right) \qquad (4)$$

where Tr(L)=1. All of them are based on the continuum theory of dielectrics. First of all the hypothesis of the isotropic local field in an anisotropic dielectric was proposed, i.e. that $f_{zz} = f_{yy}$ yielding:

$$\Delta L = \frac{1}{3}\frac{n_x^2 - n_z^2}{2n_z^2 + n_x^2 - 3} \qquad (5)$$

This model was not sufficiently well justified and later Segre[13] considered the local field in the ellipsoidal cavity arbitrarily oriented in anisotropic dielectric and concluded that:

$$\Delta L = \langle P_2^{cav} \rangle \Delta L_{cav} \qquad (6)$$

where $\langle P_2^{cav} \rangle$ is the parameter of the orientational ordering of the cavity and ΔL_{cav} is related to the ratio of the cavity axes through:

$$\Delta L_{cav} = \frac{a_1 a_2^2}{2} \int_0^\infty dv \left(v + a_2^2\right)^{-3/2} \left(v + a_1^2\right)^{-1} - 1/3 \qquad (7)$$

The lack of *a priopi* information on the parameters entering (6) can be compensated by the hypothesis that $\langle P^{cav}{}_2 \rangle \equiv \langle P_2 \rangle \propto \Delta n$ (the birefringence of the liquid crystal) and hence

$$\Delta L = \frac{\Delta n}{\Delta n_{max}} \Delta L_{cav} \qquad (8)$$

where Δn_{max} is the value of birefringence extrapolated to zero temperature (perfect orientational order). Equations (4) and (8) enable the local field anisotropy determination from the refractometric data.

The alternative way is to measure the local field anisotropy experimentally. Several approaches were proposed for this and the relevant data for some substances are available in the literature[10,14-16]. It has been shown that structural anisotropy is not proportional to the order parameter, but is rather its linear function. The proportionality coefficient, ΔL_{cav}, has been also estimated from these studies and has been shown to be strongly dependent on the molecular shape. The closest to our system compound studied by resonance Raman scattering is 5CB, which has amyl instead of alkoxy chain and for which:

$$\Delta L = A + B\Delta n, \quad \text{where } A = 0.011, B = -0.204. \qquad (9)$$

We recalculated these data for our system leaving A unchanged and increasing $|B|$ according to the increase of the molecular length from 19.8 for 5CB to 23.5 for our mixture (according to [9] molecular length of 8OCB is 2.4 nm and that of 6OCB is 21.9 nm) using equation (7). The resulting B= -0.210 was used for the calculations of the the local field anisotropy in the studied mixture.

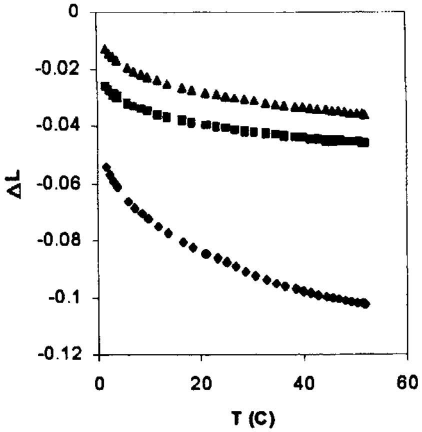

FIGURE 2 Structural anisotropy of the mixture 8OCB-6OCB calculated by different methods: ◊ - according to equation (8) (Δn_{max}=0.332, ΔL_{cav}= −0.152); Δ - according to equation (9) (A=0.011, B= -0.210); ◻ - in the isotropic local field approximation (equation (5)).

Structural anisotropy calculated by the aforementioned methods is shown in Figure 2. It is seen, that assumption of proportionality of ΔL and ΔL_{cav} results in the structural anisotropy values substantially deviating from the other two approximations. Actually, so high structural anisotropy has been never observed experimentally [14-16]. So, to be self-consistent we use equation (9) for the structural anisotropy estimation for treating all our experimental data.

After correcting Raman depolarization ratios for the local field anisotropy and the distortion of the scattering volume (see equations (3)) one can determine the orientational order parameters assuming axial symmetry of the polarizability derivatives tensor in formulae (1)-(2). Axial symmetry is almost obvious for the cyano fragment stretching, but for the benzene ring mode this can be rather severe approximation. Nevertheless we used it to determine parameter a from depolarization ratio in the isotropic phase and the results of the order parameters computations in this approximation are presented in Figure 3.

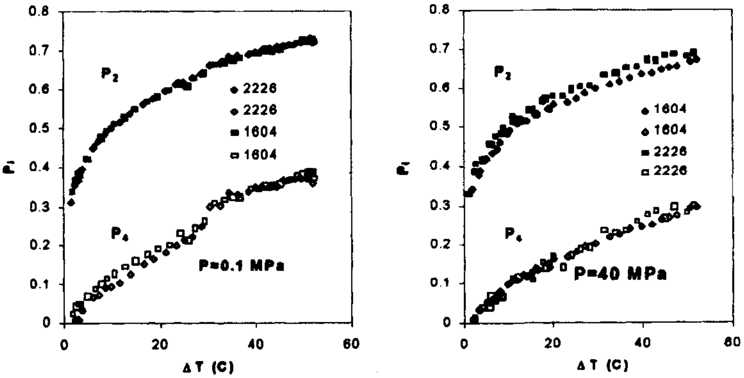

FIGURE 3 Orientational order parameters as a function of temperature for two different pressure values determined from Raman depolarization ratios of cyano fragment stretching (line at 2226 cm^{-1}) and benzene fragment mode (line at 1604 cm^{-1}) assuming axial symmetry of their polarizability derivatives tensors.

Good coincidence of the order parameters for both intramolecular modes may be either occasional, or can be a sign of the axial symmetry of the benzene ring mode for cyanobiphenyl derivatives. There are some arguments in favour of the last statement. Certainly, in pure benzene the symmetry axis of this mode is perpendicular to the plane of the ring[17]. But in biphenyl the planes of two rings are twisted to the angle 30-45°. Due to this the components of this mode perpendicular to the biphenyl linkage are partially averaged. The presence of para-substituted cyano fragment increases conjugation and increases substantially the component of the polarizability derivative tensor parallel to the biphenyl linkage so that the difference of the other two components becomes negligible. Nevertheless, to check consistency of these arguments we calculated the third independent Raman depolarization ratio in the mesophase, R_3, with the excitation beam polarized perpendicularly to the nematic optical axis and compared it with the experimentally measured one at ambient pressure (see Figure 4).

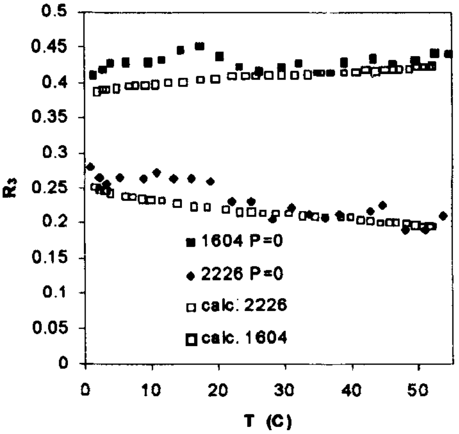

FIGURE 4 Experimentally measured and calculated (in approximation of axial symmetry of the polarizability derivative tensor) Raman depolarization ratio R_3 for two Raman bands (marked in the legend) at ambient pressure.

It is seen that coincidence of the experimetal data with formula

$$R_3 = \frac{I_{yx}}{I_{xx}} = \frac{3a^2\left(7 - 10\langle P_2\rangle + 3\langle P_4\rangle\right)}{70 - 70\sqrt{2}a\langle P_2\rangle + a^2\left(28 - 20\langle P_2\rangle + 27\langle P_2\rangle\right)} \qquad (10)$$

is rather good in the SmA and N_r phases. Somewhat higher experimental values in N phase are probably due to scattering and consequent depolarization of light on the long-wave fluctuations of the nematic optical axis[18] (R_3 measurements were done in the cells 15-17 μm thick). Biaxiality of the polarizability derivative tensor and its tilt in the molecular frame can not explain such deviations. Therefore, some deviations of the R_3 from the values calculated in the uniaxial approximation were neglected and the order parameters presented in Figure 3 are considered to be sufficiently accurate.

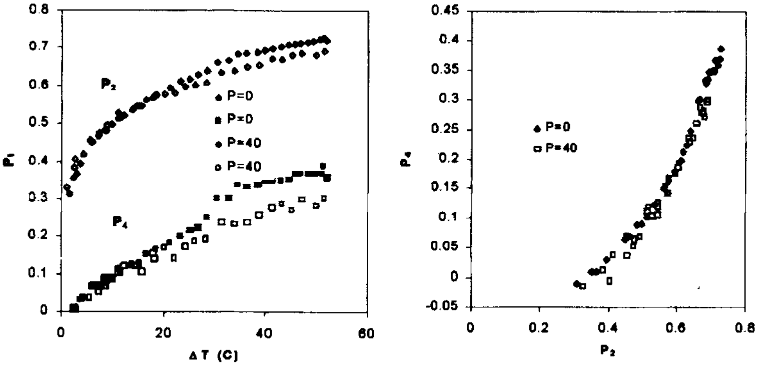

FIGURE 5 Temperature dependence of the orientational order parameters determined from depolarization ratios of 2226 cm^{-1} Raman line. The pressure is shown in the legend.

It is interesting to compare the temperature behaviour of the orientational ordering at different pressure values (see the left part of Figure 5, where the results of Figure 3 are presented in another way). It is seen that while in the nematic phase both $\langle P_2 \rangle$ and $\langle P_4 \rangle$ do not depend on pressure, in SmA and N_r phases which are observed only at ambient pressure $\langle P_2 \rangle$ is considerably higher. In principle, this can mean increase of the fluctuations of the molecular orientational disorder:

$$\delta\langle P_2 \rangle = \langle P_2^2 \rangle - \langle P_2 \rangle^2 = \frac{1}{5} + \frac{2}{7}\langle P_2 \rangle + \frac{18}{35}\langle P_4 \rangle - \langle P_2 \rangle^2 \qquad (11)$$

which increases with increasing $\langle P_4 \rangle$. But if one compare variation of the order parameters in other coordinates (right part of Figure 5) it comes clear, that their temperature and pressure dependence both can be explained in the framework of a single mean field model[6] and do not require introduction of any additional molecular pretilt due to

antiferroelectric packing of the nearest neighbours in the SmA, or N_r phase.

Acknowledgements

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