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Raman studies of some cyanobiphenyl derivatives under pressure

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We present the results of an experimental study of the Raman depolarization ratio for the cyano stretching mode in two mesogens, 5CB and 80CB, under variable temperature and pressure. In contrast to previous observations, the Raman results do not yield any indication of molecular association, even in such an expectedly strongly associated liquid crystal as 80CB, which has a re-entrant nematic phase at elevated pressure. Possible explanations for this are discussed.

1. Introduction and background

Electrostatic interactions are recognised as playing a rather important role in mesophase formation. The presence of a strong molecular permanent dipole moment influences both the electric and thermodynamic properties of the mesophase. Interactions of polar molecules resulting in a particular molecular ordering are considered to be responsible for a variety of smectic A phases [1] and for induced smectic and re-entrant phenomena [2]. The existence of a ferroelectric smectic C* phase is recognised as being due to biased molecular rotation around the long axis caused by molecular polar interactions [3]. Usually, manifestations of molecular association due to dipole-dipole forces are studied by measuring the dielectric properties and are analysed in terms of the Kirkwood g_1 factor [4]. If molecular association can modify the phase diagram, then one may expect that it changes not only the local molecular arrangement, but also the long range orientational ordering. Comprehensive information on long range orientational ordering is contained in the orientational distribution function. Therefore, by studying various orientational order parameters, i.e. expansion coefficients of the orientational distribution function into a Legendre polynomials set, one can get some insight into the specific consequences of molecular polar interactions.

Raman scattering has proved to be a very powerful tool in studying orientational ordering in liquid crystals [5–7]. This method is based on measurements of the 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 scattering light, respectively. The ratios of the light intensities scattered with different polarization depend not only on the form of the molecular polarizability derivatives tensor $\partial\alpha/\partial Q$, but also on the orientational ordering of the relevant intramolecular fragment and, in particular, on the orientational order parameters P_2 and P_4 . For example, for a symmetric intramolecular mode in a uniaxial medium consisting of axially symmetric molecules one can write:

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

$$r_2 = \frac{I_{zx}}{I_{xx}} = \frac{6a^2(7 + 5\langle P_2 \rangle - 12\langle P_4 \rangle)}{140 - 140\sqrt{2}a\langle P_2 \rangle + a^2(56 - 40\langle P_2 \rangle + 9\langle P_4 \rangle)} \quad (2)$$

where a is a dimensionless ratio of the 2 components (one can call it anisotropic to isotropic) of the molecular polarizability derivative tensor for a particular intramolecular mode in a cyclic basis set [8]:

$$a = (\partial\alpha_2/\partial Q)/(\partial\alpha_0/\partial Q) \quad (3)$$

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and it is related to the Cartesian components by the formulae

$$\alpha_{00} = -(\alpha_{kk} + \alpha_{mm} + \alpha_{nn})/\sqrt{3}, \alpha_{20} = (\alpha_{kk} + \alpha_{mm} - 2\alpha_{nn})\sqrt{6} \quad (4)$$

where k, m, n denote the principal axes of the molecular fixed system. In equations (1) and (2), x, y, z are the axes of the laboratory system with z being the symmetry axis of the mesophase (similarly to the definitions in [5]). Coefficient a is usually determined from measurements on the isotropic phase, and consequently, using equations (1) and (2), one can investigate P_2 and P_4 for 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 in [5] and we refer the reader to that paper for detailed explanations.

Several intramolecular modes were found to be very convenient for orientational ordering studies. Among them is the cyano stretching mode, which is well localized in the molecule, far separated from other modes in the frequency spectrum and has a convenient (uniaxial) Raman tensor. Cyanophenyl derivatives have already been studied by Raman scattering [5–11] and rather interesting phenomena were observed, leading to contradictory conclusions. Some authors (see, for example, [6]) interpret the non-trivial behaviour of the order parameters, obtained from experimentally observed depolarization ratios, as being influenced by molecular association. Others [10] bring strong arguments against this, because cyano-containing tolans and phenylcyclohexanes do not show a negative P_4 . All of them agree on one point: more detailed studies combining different methods are necessary to arrive at a definite conclusion as to whether antiparallel packing of molecules can be observed by the Raman scattering technique or not.

Measurements of the material properties under elevated pressure open another dimension in studying phase diagrams. Orientation order parameters, which are usually measured as a function of temperature, can also be studied as a function of pressure [12]. In fact, for some cyanophenyl derivatives it was observed that while at constant pressure the temperature variation of the orientational order parameter, derived from refractometric measurements, describes the behaviour of the dielectric susceptibilities well, this is not the case for varying pressure [13, 14]. In addition, decrease in activation enthalpy and volume with an increase in temperature and/or pressure within the nematic phase of these cyanophenyl derivatives were observed by dielectric relaxation

studies [13, 15]. The most probable interpretation of these results (for different homologous sets of substances they are discussed in the review [16]) is based on the variation of the local antiparallel molecular alignment under elevated pressure as dimers disappear. On the other hand, the appearance of re-entrant phenomena [2] can be related to an increasing number of associates on increasing the pressure or decreasing the temperature. Additional experimental observations are clearly necessary to verify which of these two opposite tendencies is correct.

In any case, given the local ordering changes, one can expect that not only g_1 , but also other order parameters will be changed. The only problem is the observation of this effect, because one cannot directly compare the pressure dependence of P_2 with its temperature dependence. Raman measurements help to avoid this problem. When P_2 and P_4 are determined simultaneously, one can study P_4 not simply as a function of the parameters of the state, but as a function of P_2 in different states. One can derive such a dependence also from molecular statistical theories. For example, in that proposed by Faber [17], molecular orientational disordering is attributed to the fluctuations of the nematic director field, the elastic properties of which are determined by the elastic constants of the liquid crystal. Analysis of the effect of such fluctuations [17] has shown, that:

$$\ln(1/P_n) = \frac{n(n+1)}{4} X \quad (5)$$

where X is the sum of the mean square values of director fluctuations over all modes. And, in particular, for the order parameters of interest one obtains:

$$P_4 = P_2^{10/3}. \quad (6)$$

This relation (or a somewhat different one in another theory) is valid for a single molecule. If there is any contribution of the antiparallel packing to the decrease in P_4 values, one should be able to observe differences in the P_4 versus P_2 dependencies under variable temperature or pressure.

For our studies we have chosen typical substances for which the effect of molecular association has been already observed, namely 4-pentyl-4'-cyanobiphenyl (5CB) and 4-octyloxy-4'-cyanobiphenyl (80CB). The first liquid crystal possesses only a nematic mesophase, while the latter shows smectic A as well as nematic phases at different temperatures, indicating stronger hard core interactions. At elevated pressure a re-entrant nematic phase was observed for 80CB [2], pointing towards substantial variations of the molecular association.

Keeping this in mind, our main aim was to prove whether changes in the local molecular arrangement can be detected by means of measurements of Raman depolarization ratios under pressure.

2. Experimental

Raman scattering was excited with the Argon-ion laser lines at 514 and 497 nm, with 15–50 mW power incident on the sample. The use of the second line enabled substantial suppression of the fluorescent background, arising from the windows of the high pressure cell, and consequently an increased signal-to-noise ratio. The light scattering spectra in the back scattering geometry were registered by a Spex-Ramalog spectrometer model 14018. For achieving a high signal-to-noise ratio, the spectral slit-width of the monochromator was chosen to be comparatively large: 4.4 cm^{-1} . Depolarization ratios were checked with CCl_4 lines. Further spectroscopic details of the experimental arrangement and the methods used for measuring the Raman intensities can be found in [18].

The liquid crystal was aligned between two fused silica windows with inner surfaces covered with AL3046 (JSR) 20 nm thick aligning films unidirectionally rubbed. The cell was not completely sealed, to allow equilibration of internal and external pressures. To prevent pollution of the liquid crystal by the pressure conducting fluid, the central part of the quartz cell was separated from the filling window by a snake-like path, 1–2 mm wide and 10–15 mm long. Such a configuration of the cell enabled Raman measurements under elevated temperature and pressure without noticeable uptake of impurities for several days. The purity of the liquid crystal substances was verified periodically by checking the phase transition temperatures and the increase of the fluorescence background.

For measurements under pressure, the specimen was placed inside a cylindrical autoclave made of stainless steel ($p_{\text{max}} = 200 \text{ MPa}$) with an external heating system (a detailed description and drawing can be found in [19]). The autoclave was closed from both sides with bevelled screws which served as holders for the synthetic sapphire windows. The supplementary inlets for the pressure transducing fluid and a thermocouple were placed in the cylindrical surface of the autoclave. One inlet was connected to a Dunze high pressure apparatus for applying and measuring pressure. Silicon oil PH300 was used as the compressing fluid. Under pressure, the fluid directly penetrated into the quartz cell, as was observed using crossed polarizers, ensuring identical pressure inside the cell and at the manometer. Both, the exciting beam and the scattered light passed through the front sapphire window of the high pressure cell, which was cut with its optical axis perpendicular to the

beam direction. Within the pressure and temperature ranges used in the present experiments no strain-induced variations of the optical axis of the windows was observed. To enable depolarization ratio measurements, the specimen was oriented with its optical axis parallel to that of the front sapphire window. In order to prevent distortion of the light and to reduce the fluorescence background of the silicone oil, the specimen was directly attached to the front sapphire window and a fused silica cylinder was inserted additionally between the specimen and the rear autoclave window, passing the outgoing excitation beam.

The temperature was measured by a thermocouple sealed in the autoclave and placed close to the specimen. Reproducibility and the precision of the pressure–temperature conditions were checked by observing the isotropic–nematic phase transitions and comparing the result with the phase diagrams presented in [2, 13, 15, 20 21]. The reproducibility of the pressure p and the temperature T was better than $\pm 1 \text{ MPa}$ and $\pm 0.3 \text{ K}$, respectively.

3. Results and discussion

Depolarization ratios of 5CB and 80CB were measured within the interval of existence of the nematic and smectic phases. The measurements of the depolarization ratios were performed for the cyano stretching mode (2227 cm^{-1}) at several elevated temperatures (with varying pressure) and the results are presented in figures 1 (a) and 2 (a). We did not find any pressure or temperature dependence of the depolarization in the isotropic phases. In all cases the depolarization ratio was within 0.26–0.27, in good agreement with the data available in the literature [6, 10]. For all further calculations we used 0.265. Reproducibility of the data for the mesophase and of the temperature–pressure conditions was checked by repeated measurements using different cells. The possible influence of artefacts on the polarization measurements was checked with various orientations of the cell relative to the spectrometer (and consequently to the illuminating system) and using the thermostating system without sapphire windows. The cell thickness was within 5–10 μm (measured interferometrically) and no thickness corrections of the resulting depolarization ratios were applied. The scatter of the individual measurements, if not very close to the phase transition, is estimated to be $\pm 5\%$.

Variable temperature measurements, presented in parts (b) of figures 1 and 2, were also done and can be compared with the data available in the literature [6, 10]. We noticed, that R_2 coincides rather well with the data available on 5CB, while R_1 is systematically lower in our case (about 0.02 far from the nematic to isotropic phase transition). Such a difference is hard to explain by any misalignments in our experimental set-up,

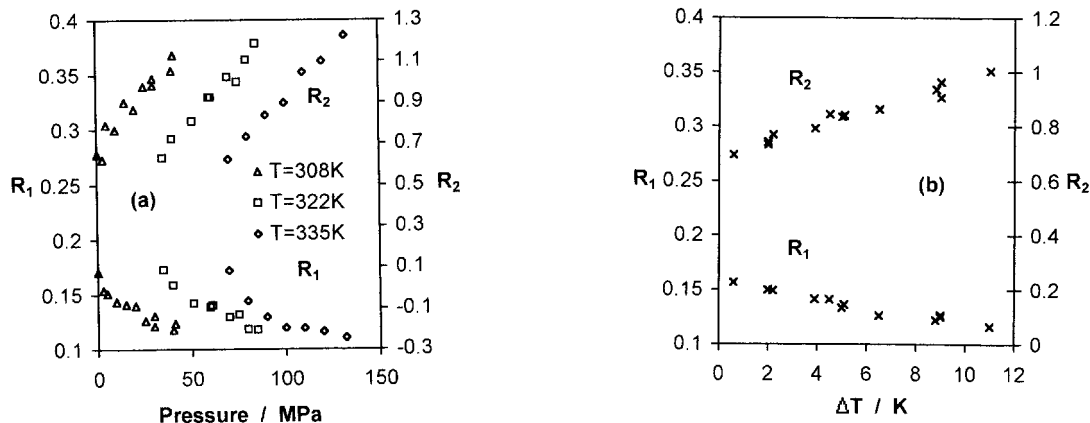


Figure 1. Pressure (a) and temperature (b) dependence of Raman depolarization ratios for the 2227 cm^{-1} line of 5CB. Temperature values are displayed in (a) and $p = 0$ in (b). Temperature in (b) is $\Delta T = T_{\text{NI}} - T$ measured relative to the nematic–isotropic phase transition $T_{\text{NI}} = 308.5\text{ K}$.

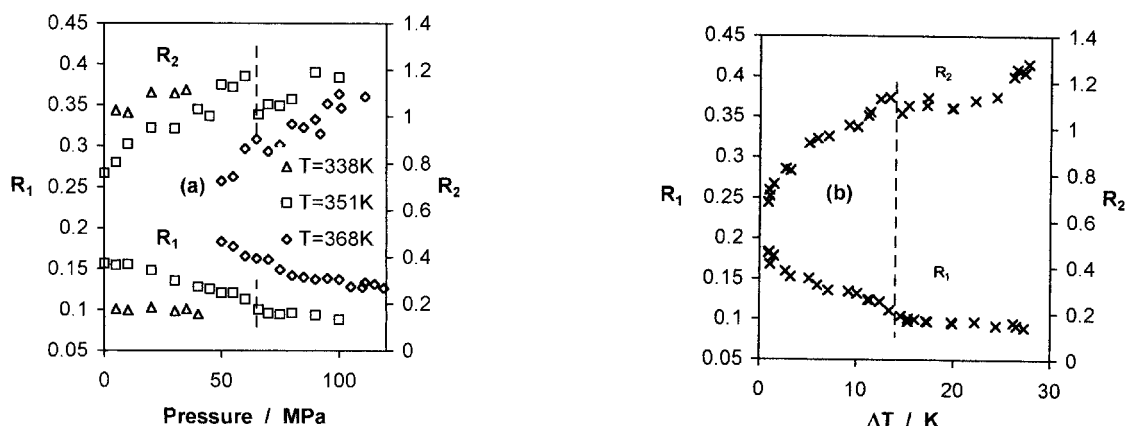


Figure 2. Pressure (a) and temperature (b) dependence of Raman depolarization ratios for the 2227 cm^{-1} line of 80CB. Temperature values are displayed in (a) and $p = 0$ in (b). Temperature in (b) is $\Delta T = T_{\text{NI}} - T$ measured relative to the nematic–isotropic phase transition $T_{\text{NI}} = 353.5\text{ K}$. Dashed lines show the smectic–nematic phase transitions.

because any misalignment should lead only to additional depolarization. The only explanation we have at present is a difference in the solid angle in which the scattered radiation was collected. In our case this angle was rather small (about 0.1 srad), while there are some indications [10] that in previous measurements the angle was maximized. In our experience this can substantially depolarize lines with a low depolarization ratio, having no influence on the depolarized lines. The temperature dependent depolarization ratios for 80CB can be compared with the results presented in [22]. Unfortunately, even for the isotropic phase, the data from [22] are not consistent with the other data available in the literature for the cyano stretching mode in cyanobiphenyls.

Experimentally measured Raman depolarization ratios, before being used for determining order parameters with

equations (1) and (2), are subject to recalculations:

$$R_1 = C_n \frac{f_{xx}^2}{f_{zz}^2} r_1 \quad (7)$$

$$R_2 = \frac{1}{C_n} \frac{f_{zz}^2}{f_{xx}^2} r_2. \quad (8)$$

Correction factors, C_n and f_{ii} have different meanings [5]:

$$C_n = \frac{(n_g + n_z)^2}{(n_g + n_x)^2} \quad (9)$$

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

$$f_{ii} = 1 + L_{ii}(n_i^2 - 1) \quad (10)$$

is the local field factor, accounting for the anisotropy of the electric field acting on a molecule in an anisotropic medium when an isotropic external field is applied to it. It depends not only on the optical anisotropy of the mesophase, but also on its structural anisotropy, described by the Lorentz tensor L [23]. $\text{Tr}(L)=1$ and in a uniaxial medium only the anisotropy of the molecular distribution along the symmetry axis and perpendicular to it, $\Delta L = (L_{zz} - L_{xx})/3$, influences the local field anisotropy. As is seen from these equations, besides depolarization ratios, also the refractive indices and Lorentz tensor anisotropy are required to determine the order parameters P_i . To avoid additional sources of errors we do not intend to use the isotropic local field approximation, as is often done [5, 6].

Refractive indices of 5CB in all thermodynamic states of interest can be found in [20]. We neglect the difference between the indices at 589 nm and at the wavelength of the scattered light (582 nm in our case). The data on the anisotropy of the Lorentz tensor are available only for $P = 0$ [24] and to obtain local field anisotropy corrections at elevated pressure we used the hypothesis of a linear relation between the ΔL and the birefringence [25]. We checked this for variable temperature and found that the relation $\Delta L = -0.204\Delta n + 0.011$ is followed very closely for 5CB.

The resulting values of the orientational order parameters are presented in figure 3. It is seen that the shape of the curves is rather similar for both variable pressure and temperature plots. The values of P_2 are in good agreement with those derived from the refractive indices [20, 26], at least far from the melting point. As

mentioned in [12], the pressure readings in [20] are systematically shifted (about 10%) to higher values. This means that the curves in figure 3 (a) are probably to be shifted slightly to the left. Anyway, no essential difference of the deviations from our results is noticeable between the pressure and temperature dependences, as was found for dielectric measurements [13]. To examine more closely to which changes of the orientational distribution function variation of the thermodynamic state leads, we plotted P_4 versus P_2 . As seen from figure 4, within experimental error the curves for all temperatures with

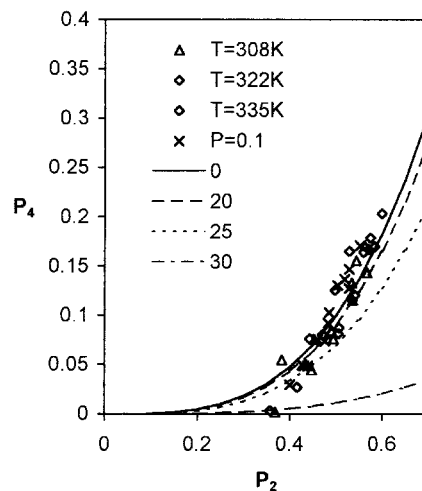


Figure 4. P_4 vs P_2 dependence for 5CB. The results are recalculated from both the pressure and the temperature dependence of the depolarization ratios, as displayed in the figure. The curves show predictions from Faber theory [17] for different values of the cyano bond tilt (indicated in degrees in the legend) in the dimer, as explained with equations (5, 6, 11).

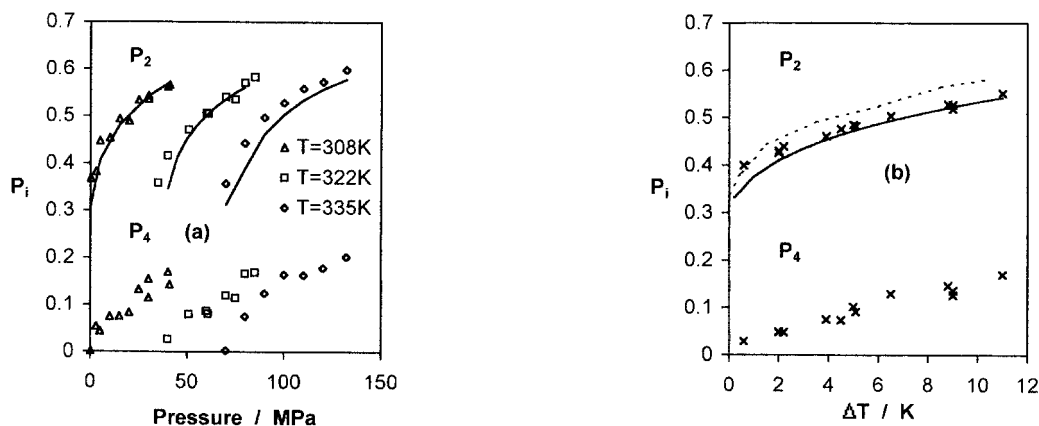


Figure 3. Pressure (a) and temperature at $p = 0$ (b) dependence of the orientational order parameters of 5CB derived from Raman depolarization measurements presented in figure 1. The value of the constant parameter (temperature in part a) is displayed in (a). The order parameters are derived with equations (1–4) and (7–10) as explained in the text. The solid curves are for the order parameters calculated from the refractive indices [20, 26]. The dashed curve represents the data from [28].

variable pressure coincided with the curve for variable temperature.

The nature of the expected changes and differences could be understood on the basis of the following scheme. Molecular orientational ordering in nematics can be described as a result of the action of some average orienting field due to the neighbouring molecules (pseudo-potential of the mean-field theories [27]), or due to partial disorder of the perfectly aligned molecular field caused by agitation through thermal fluctuations [17]. In any case, a single molecule is treated as a unit to be oriented and theories of the liquid crystal state deliver relations between orientational order parameters (an example of such relation can be found in the introduction). If any dipole–dipole association is expected to be in the form of dimers, the dimers play a role as such units orientationally aligned by the molecular field. The long axes of the constituent molecules may not be parallel to the long axis of this unit (see, for example, figure 5). If the angle between these axes is β , then the order parameter of the molecular long axis (indexed mol) is related to the order parameter

of the associate (indexed ass) via [8, 17]:

$$\langle P_n^{\text{mol}} \rangle = \langle P_n^{\text{ass}} \rangle P_n(\cos \beta). \quad (11)$$

It is evident, that the higher the rank of the order parameters, the stronger it is reduced by molecular association. This effect is illustrated by the curves in figure 4. It is also evident from the figure that the effect is observable in our case for a sufficiently strong inclination of the molecular long axis in such an associate. In fact, our experimental data, although scattered, correspond better to the curves with zero or very low tilt (the difference of this plot from figure 22 in [5] is due to differences in the depolarization ratios, as mentioned before, because the local field anisotropy correction has a minor effect). The explanations for this can be various. On the one hand, as shown in figure 5, due to molecular flexibility, the tilt of the hard core and consequently of the cyano bond relative to the long axis of the dimer can be rather small. On the other hand, such behaviour of the experimental order parameters can mean that antiferroelectric local packing of the molecules has a statistical character and does not imply a kind of dimerization. If a molecule has no preferable pairing, but more or less interacts similarly with the surroundings, the g_1 Kirkwood factor for such a system may be rather small, but this will not lead to a substantial decrease of P_4 relative to P_2 . This explains also the experimentally observed fact (see figure 4) that for 5CB the relation $\ln(P_4)/\ln(P_2) = 10/3$ (derived for single molecule distribution) holds. Other explanations of the Raman data, such as the absence of antiparallel orientation of neighbouring molecules, or small variations of the degree of association are inconsistent with the experimental results reviewed in the introduction.

In fact, to check the effect of molecular association, it is not necessary to perform every time all the recalculations from the depolarization ratios to the orientational order parameters. R_1 and R_2 are not similarly sensitive to the variations of P_2 and P_4 . As seen from figure 6, R_2 is

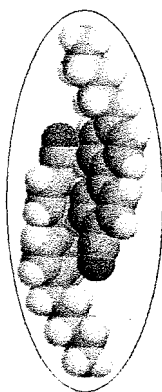


Figure 5. Schematic representation of a dimer of 5CB. The surrounding ellipsoid shows the shape of the new single unit to be aligned by the nematic field.

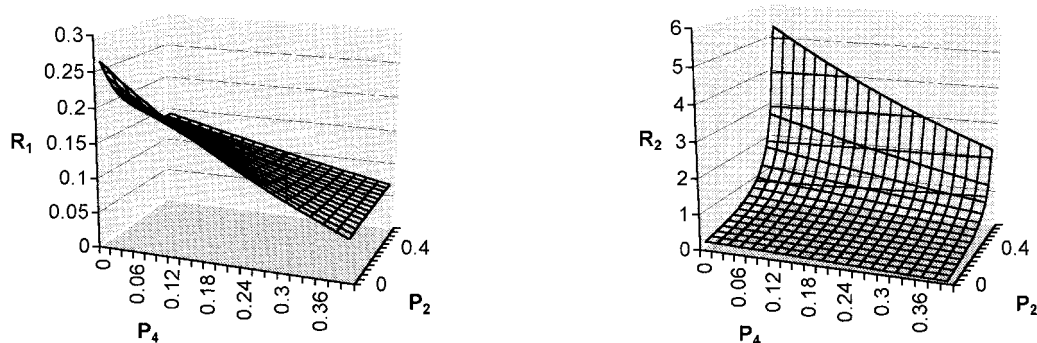


Figure 6. Dependence of the two Raman depolarization ratios for the 2227 cm^{-1} line ($\rho = 0.265$ in the isotropic phase) on the orientational order parameters.

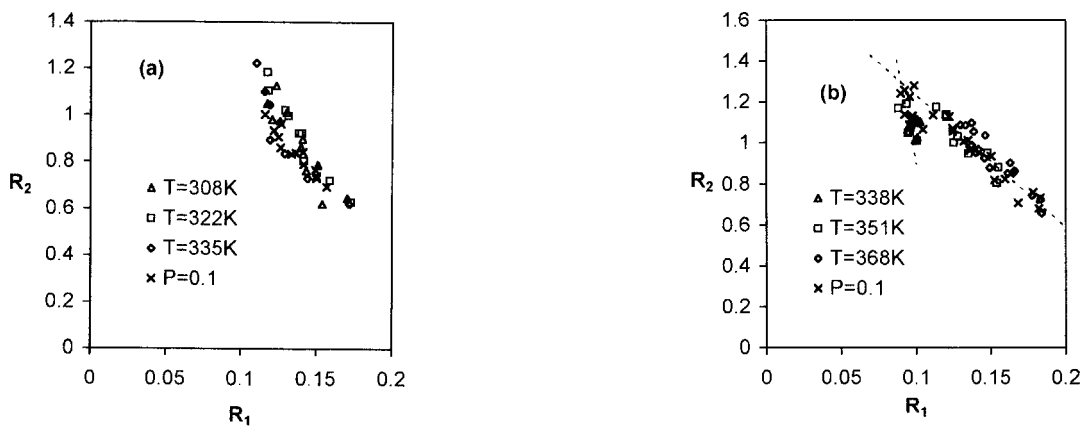


Figure 7. R_2 vs R_1 dependence for 5CB (a) and for 80CB (b). The results are presented for both pressure and temperature dependence of the depolarization ratios as displayed in the figures. Dashed lines in (b) are shown for guidance to distinguish smectic and nematic data.

more sensitive to the variations of P_2 than is R_1 . Even more, as evident from figure 6 (a), depending on the value of P_4 , R_1 can either increase or decrease with increasing P_2 , while variation of P_4 produces almost proportional changes of both ratios. Formation or dissipation of the dimers lead to the variation of both order parameters, but one of the ratios, namely R_2 , would be more strongly influenced by these changes and would evidence the process taking place at the molecular level. Therefore, verification of the changes of the orientational distribution function can be obtained by the straightforward comparison of the R_2 versus R_1 variation under different thermodynamic conditions. As can be seen, the variable pressure and variable temperature data in figure 7 coincide, as they do in figure 4. This yields confirmation that some approximations used during recalculation of the experimental results did not influence the general conclusions. Strong deviations from the theoretical predictions are observed only for the smectic phase of 80CB, as could be expected, because the curves presented in this figure were calculated on the basis of the theory of nematics. Nevertheless, even in the smectic phase, variable pressure data coincide with those for variable temperature. In fact, depolarization ratios in the smectic phase should be much more sensitive to any kind of molecular inclination (caused by dimerization) because of higher molecular ordering in the smectic phase in comparison with the nematic phase. On the contrary, quite similar pretransitional effects and similar ordering are indicated by the Raman measurements under both temperature and pressure variation.

4. Conclusions

The present studies of the pressure and temperature dependence of the Raman depolarization ratios show that, within the experimental uncertainty, the degree of

molecular dimerization under variable pressure is the same as that observed under variable temperature. There are two explanations for this which are consistent with other experimental data on the substances studied. First of all, for several reasons such as conformational flexibility, molecules forming dimers may remain with their hard cores preferentially parallel to the nematic or smectic director. Secondly, molecular association in mesogenic cyano compounds probably does not resemble a true dimerization, at least in the sense of the absence of stable pairs which can be distinguished from the rest of the molecules by the energy of their interaction; rather we have two or more molecules surrounding a central one and having their dipoles antiparallel to it. On the other hand, these studies have shown that the molecular association does not influence the Raman depolarization ratios to such an extent that the P_4 order parameter obtained from them can become negative.

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