Hydrocarbon Chain Ordering in Liquid Crystals Investigated by Means of Infrared Attenuated Total Reflection (IR-ATR) Spectroscopy

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Stationary and modulated IR-ATR spectra of Schiff’s base nematic liquid crystals are reported. The mean order parameter of both, the aromatic core and the hydrocarbon chains is determined by analysis of the infrared dichroism of characteristic absorption bands. Hydrocarbon chain ordering was found to be considerably lower than predicted by Marčelja’s statistical theory.

1. Introduction

Even-odd alterations of characteristic parameters depending on hydrocarbon chain length such as nematic-isotropic and smectic-isotropic transition temperature, nematic-isotropic transition entropy and core order parameter have been measured in homologous series of liquid crystals. The alterations found correspond to the even-odd behaviour of entropy, and melting and boiling temperatures of n-parafins.

Recent calculations by Marčelja 4 based on the Maier-Saupe theory 5 take the interactions between hydrocarbon chains as well as those between hydrocarbon chains and aromatic cores of liquid crystals into account. Good agreement between calculated and measured core order parameters was found in homologous series of p-alkoxyazoxoxybenzenes 3 using Marčelja’s theory. However, discrepancies arise between theory and experiment when comparing order parameters of methylene groups in the hydrocarbon chains. Recent studies of deuteron magnetic resonance 6, 7 showed a faster decrease of CH 2-order parameter than should be expected from theory 4 when moving from the rigid core along the hydrocarbon chain.

We shall report on measurements using attenuated total reflection (ATR) infrared spectroscopy to study order parameters of alkyl cyano Schiff’s base 8 liquid crystals. Reorientation of the strongly positive dielectric 9 liquid crystal molecules under the influence of electric fields and the consequent changes occurring in the IR-ATR spectra are investigated. Measurements of core order parameter and chain mean order parameter are compared with calculations based on molecular field theory 3. Our results — which are in good agreement with experimental findings reported by Deloche et al. 6, Emsly et al. 7 and Maier and Englert 10 — show nearly random orientation of the CH 2-groups in the hydrocarbon chains 11. This finding is contradictory to theoretical predictions made by Marčelja 4.

2. Experimental

2.1. ATR-Spectra

For a general review of ATR-technique the reader is referred to reference 12.

2.1.1 Stationary ATR spectra were recorded on a Perkin Elmer Mod. 225 infrared spectrometer equipped with two ATR attachments (Wilks Sci. Corp. Mod. 9 and 50). The reflection plates were germanium (50 × 20 × 1 mm) supplied by Harrick Sci. Corp. The angle of incidence was 30° resulting in about 25 active reflections. Polarization measurements were made using a Perkin Elmer grid polarizer. A schematic diagram of the ATR geometry used is depicted in Figure 1.

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2.1.2. Modulated Excitation ATR Spectra (ME-ATR)

Several publications have been reported describing the principle of modulation spectroscopy. The technique can always be applied provided the system studied allows periodic excitation. ME-spectroscopy enables selective scanning of those absorption bands of the infrared spectrum resulting from molecules (or parts of them) that are involved in the stimulated processes. All absorption bands which are not affected by excitation are suppressed. The frequency dependence of signal amplitude and phase lag between stimulation and detected infrared signal is typical for the kinetics involved.

Figure 2 shows a diagram of the ATR-spectrometer. A gated 500 Hz sine-wave voltage (1:1 duty cycle, 4 Hz frequency, 40 volts) was used to realign the liquid crystal molecules in the electric field. For a more detailed description of the apparatus the reader is referred to reference 14.

2.2. Preparation of Liquid Crystal Samples

The long axis of the liquid crystal molecules were aligned parallel to the $y$-axis (Fig. 1) to get maximum change of polarized ATR-IR-absorption when reorienting the molecules under the influence of an applied electric field. Alignment was initiated by polishing both, the germanium internal reflection plate (electrode E1) and the SnO$_2$ coated glass plates (electrodes E2) parallel to the $y$-axis (Figure 2). Electrodes E1 and E2 were separated by 20 $\mu$m mylar spacers. Spontaneous parallel alignment of the liquid crystal molecules occurred when filling the electrode sandwiches by capillary action. The homogeneity of molecular alignment could be enhanced by heating up the cells to $\sim 10$°C above the nematic-isotropic transition temperature $T_c$ and cooling it slowly down again. Applying a voltage to the electrodes E$_1$ and E$_2$ (Fig. 2) caused the long axis of the positive dielectric molecules to realign parallel to the electric field, i.e. parallel to the $z$-axis.

2.3. Chemicals

The liquid crystal used was RO-TN-200, a mixture of 1 part of 4-(4'-n-propylbenzylidene amino)-benzonitrile and 2 parts of 4-(4'-n-hexylbenzylidene-amino)-benzonitrile with a nematic temperature range of $\sim -15$°C to 65 °C. The substance was supplied by F. Hoffmann-La Roche, Ltd., Basel.

3. Results and Discussion

3.1. Assignment of Infrared Absorption Bands

Extensive investigations of liquid crystals using conventional infrared transmission spectroscopy were reported by Maier and Englert 10, 15 and Maier and Markau 16. The assignment of some prominent absorption bands is listed in Table 1.

It was shown that vibrational coupling between the two benzene rings of the aromatic core of liquid crystal molecules is weak 15. Therefore, only the local C$_{2v}$ symmetry of one ring has to be considered when estimating the direction of the transition dipole moment. Consequently two directions of transition moments of typical benzene ring vibrations have to be expected, namely parallel and perpendicular to the direction of the para-axis of the aromatic core.

3.2. Molecular Ordering in the Liquid Crystalline State

3.2.1. Stationary ATR-Spectra

Molecular ordering can sensitively be detected by using polarized ATR-spectroscopy (Fig. 1). The reader is referred to reference 17 for a detailed discussion of analysis of polarized spectra.

Liquid crystal molecules are randomly oriented in the isotropic phase above the transition temperature $T_c$. The spectra in Fig. 3a — recorded at 70 °C > $T_c$ — nevertheless show distinct polarization. This polarization effect is a typical feature of
Table 1. Assignment of some typical infrared absorption bands of RO-TN-200.

<table>
<thead>
<tr>
<th>Wavenumber [cm(^{-1})]</th>
<th>Assignment</th>
<th>Direction of dipole moment relative to para-axis</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>2960</td>
<td>(\nu_{as}(\text{CH}_3))</td>
<td>weakly polarized (^2)</td>
<td>antisymmetric CH(_3) stretch</td>
</tr>
<tr>
<td>2930</td>
<td>(\nu_{as}(\text{CH}_2))</td>
<td></td>
<td>antisymmetric CH(_2) stretch</td>
</tr>
<tr>
<td>2871</td>
<td>(\nu_{s}(\text{CH}_2))</td>
<td></td>
<td>symmetric CH(_2) stretch</td>
</tr>
<tr>
<td>2858</td>
<td>(\nu_{s}(\text{CH}_3))</td>
<td></td>
<td>symmetric CH(_3) stretch</td>
</tr>
<tr>
<td>2202</td>
<td>(\nu(C=N))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1630</td>
<td>(\nu(C=C))</td>
<td>(22^\circ)</td>
<td></td>
</tr>
<tr>
<td>1598</td>
<td>(\nu(C=C))</td>
<td></td>
<td>skeletal vibration of benzene ring; Ref. (^{15, 28})</td>
</tr>
<tr>
<td>1595</td>
<td>(\nu(C=C))</td>
<td></td>
<td>skeletal vibration of benzene ring; Ref. (^{15, 28})</td>
</tr>
<tr>
<td>1495</td>
<td>(\nu(C=C))</td>
<td></td>
<td>skeletal vibration of benzene ring; Ref. (^{15, 28})</td>
</tr>
<tr>
<td>1465</td>
<td>(\delta(\text{CH}_2))</td>
<td>weakly polarized (^3)</td>
<td>methylene bending vibration</td>
</tr>
<tr>
<td>1418</td>
<td></td>
<td></td>
<td>aromatic core. Also present in 4-4'-difluoro-benzalaniline, Ref. (^{15})</td>
</tr>
<tr>
<td>1412</td>
<td>(\epsilon\nu \cdot \delta(\text{CH}))</td>
<td>weakly polarized (^3)</td>
<td>(-\text{CH} = \text{N}-\text{group} )</td>
</tr>
<tr>
<td>1375</td>
<td>(\delta_{s}(\text{CH}_3))</td>
<td>weakly polarized (^3)</td>
<td>symmetric methyl bending vibr.</td>
</tr>
<tr>
<td>1195</td>
<td>(\nu(CX) + \delta(\text{CH}))</td>
<td>stretching of para-substituents X of the benzene ring + CH-deformation, Ref. (^{15, 28})</td>
<td></td>
</tr>
<tr>
<td>1114</td>
<td>(\nu(C-C) + \gamma_{1}(\text{CH}_3))</td>
<td>weakly polarized (^3)</td>
<td>C—C-stretch of hydrocarbon chains and CH(_2)-twist (^4)</td>
</tr>
<tr>
<td>1108</td>
<td></td>
<td></td>
<td>aromatic core</td>
</tr>
</tbody>
</table>

1 Nematic liquid crystalline state.

2 Polarization not exactly determinable unless line shape analysis is performed.

3 Transition dipole moment parallel to hydrocarbon chain in the case of alltrans conformation; Ref. \(^{26, 27}\)

4 H—C—C angle deformation (CH\(_2\)- and CH\(_3\)-groups) in hydrocarbon chain; Ref. \(^{26}\).

Fig. 3 a. ATR-Spectrum of RO-TN-200 at \(T > T_c\). The molecules are not aligned. The polarization still observed is typical for perpendicular (vp) and parallel polarized (pp) ATR-spectra of an isotropic medium. \(T_c = 64^\circ\text{C}, T = 70^\circ\text{C}, \Theta = 30^\circ\).
ATR spectroscopy. It originates from the particular field configuration in the rarer medium and has nothing to do with molecular ordering. It has to be taken into account when interpreting ATR spectra.

Two principal groups of absorption bands can be distinguished (Fig. 3b) in the nematic state of RO-TN-200 ($T_{\text{meas}} = 8^\circ \text{C} < T_c$). (i) Absorption bands showing a strong change in polarization. (ii) Absorption bands showing a very weak change in polarization. The assignment of a number of ATR absorption bands shown in Fig. 3a and 3b is given in Table 1. It appears that bands related to aromatic core modes [type (i) bands] are more strongly polarized than bands assigned to typical CH$_2$-chain vibrations [type (ii) bands]. This finding is in agreement with results reported by Maier and Englert who qualitatively discussed the spectra of rotational isomers of various alkoxy chains shows that the degree of order of hydrocarbon chains must be very weak in the nematic state.

3.2.2. Modulated Excitation ATR Spectra (ME-ATR)

The dynamic ME-ATR measurements in Fig. 4 show that group (ii) absorption bands are practically absent in the spectra. This finding can be explained in two ways according to Section 2.1. Either the hydrocarbon chains remain stationary and only the polar parts of the molecules move under the reorienting influence of the applied electric field; or also the hydrocarbon chains move but possess a low degree of order, i.e. the isotropic spatial distribution of the oscillating dipoles is not influenced by the orientation process. In both cases no strong absorption bands should occur in the ME-ATR spectrum (Figure 4). However, from stationary measurements it must be concluded that only the latter case can be true. This is shown by unmodulated ATR-spectra depicted in Figure 3a, 3b and 5.

The measurements of Fig. 5 were made using the propyl and hexyl components of RO-TN-200, respec-
Fig. 5. Stationary ATR-spectrum of propyl and hexyl component of RO-TN-200 in the CH-stretching region.

They show (Fig. 5) that the absorption coefficients of $v_a(\text{CH}_3)$ and $v_s(\text{CH}_3)$ are significantly larger than the corresponding absorption coefficients of $\text{CH}_2$-group vibrations. A comparison of the band contour in the CH-stretching region of the ME-ATR spectrum (Fig. 4) with the measurements of Fig. 5 leads to the conclusion that the $r(\text{CH})$-absorption bands in the ME-spectrum are due to the propyl component of RO-TN-200. Therefore, the methyl group in C-3 position has a small degree of order thus producing only small changes of polarized absorption when reorientation of the molecules induced by an externally applied electric field occurs.

No significant contribution of the methyl group in the hexyl component of RO-TN-200 was found (Figure 5). Otherwise, the $r(\text{CH}_2)$-vibrations at 2930 and 2858 cm$^{-1}$ would have been more prominent. This leads to the conclusion that the degree of order along the hydrocarbon chain decreases very rapidly, a finding which is in agreement with recent NMR studies.$^6,7$
The dynamics of molecular alignment can be investigated by measuring the frequency dependence of signal amplitude and phase angle $\Phi$ between stimulating and detected signal using ME-ATR spectroscopy \(^{13}\) (Section 2.1.2). $\Phi$ can easily be calculated from $\tan \Phi = A_{90}/A_0$ where $A_{90}$ and $A_0$ denote the absorption coefficients measured in the 90° and 0° phase channels, respectively. A detailed kinetic analysis will be published later.

3.2.3. Measurements of the Molecular Orientation

Molecular ordering is discussed in terms of distribution functions of aromatic cores and hydrocarbon chains. In case of liquid crystals a distribution function $f(\gamma)$ for axial orientation is required where $\gamma$ denotes the angle between the direction of orientation ($y$-axis) and the para-axis of the molecules. $f(\gamma)\,d\gamma$ is proportional to the number of para-axis pointing into the conical element with symmetric angle $\gamma \leq \gamma + d\gamma$. (The reader is referred to Ref. \(^{17}\) for a detailed discussion of molecular orientation.)

The simplest molecular distribution can be described by the delta function.

$$f(\gamma) = \delta(\gamma - \gamma_0) \quad (1)$$

which means that all para-axis are oriented at a fixed angle $\gamma_0$ with respect to the $y$-axis. However, this type of distribution function is not realistic in cases where the degree of order is as low as in the hydrocarbon chains of liquid crystals. Therefore we used the Kratky distribution function \(^{17,18}\) describing the orientation changes occurring in polymers when exerting a force upon them. The model assumes that polymer chain segments are randomly oriented as long as the polymer is not stretched. In the unstretched state a volume element of side length $L'$ is defined which changes its length from $L'$ to $L$ when stretching occurs in a direction parallel to $L'$. The stretching ratio $v$ is defined as

$$v = L/L' \quad .$$

Random distribution is characterized by $v = 1$; whereas $v = \infty$ characterizes perfect ordering along the direction of stretching.

In our case parallel alignment of the liquid crystal molecules was achieved by polishing the electrode surfaces. In analogy to polymer orientation the parameter $v$ in the Kratky distribution function can be used as as measure for the quality of surface alignment of the liquid crystal molecules. The Kratky distribution function is defined as

$$f(\gamma) = \frac{v^{3/2} \sin \gamma}{(v^{-3/2} \cos^2 \gamma + v^{3/2} \sin^2 \gamma)^{3/2}} \quad (2)$$

**Calculation of the Parameter $v$**

Polarized infrared spectra enable direct determination of the dichroic ratio $R$ defined by

$$R = A_{pp}/A_{vp} \quad , \quad (3)$$

where $A_{pp}$ and $A_{vp}$ denote the absorption coefficients with respect to parallel (pp) and perpendicular (vp) polarization, respectively. Knowing $R, v$ can be determined in a straightforward way \(^{17}\). However, it must be noted that the calculations in Ref. \(^{17}\) were made for transmission measurements where all infrared electric field components are equal which is not the case for ATR measurements where the electric field is inhomogeneous (c.f. 3.2.1).

In our experiments the molecules are spontaneously aligned along the $y$-axis. The ATR dichroic ratio is then given by

$$R_{ATR} = R^T (E_x^2 + E_y^2)/E_y^2 \quad (4)$$

where $R^T$ is the transmission dichroic ratio (reduced dichroic ratio). For uniaxial orientation $R^T$ is given by \(^{17}\)

$$R^T = (\sin^2 \Theta + S')/(2 \cos^2 \Theta + S') \quad (5)$$

where $\Theta$ denotes the angle between transition dipole moment and para-axis of the molecule. $S'$ is the order parameter defined by

$$S' = \frac{\int_0^{\pi/2} \sin^2 \gamma f(\gamma) \, d\gamma}{1 - \frac{3}{2} \int_0^{\pi/2} \sin^2 \gamma f(\gamma) \, d\gamma} \quad . \quad (6)$$

$S'$ is different from the order parameter $S$ commonly used in NMR and EPR spectroscopy. However, $S$ is related to $S'$ by expression \(^{7}\)

$$S = \frac{3}{2} \int_0^{\pi/2} \cos^2 \gamma f(\gamma) \, d\gamma - \frac{3}{2} = 1 - \frac{3}{2} S'/[(1 + \frac{3}{2} S')] \quad . \quad (7)$$

Therefore, once $R_{ATR}$ has been determined $S'$ can be calculated using Eqs. (4) and (5). $v$ can be determined from Eqs. (2) and (6), i.e. from plotting $S'$ versus $v$ (c.f. Ref. \(^{17}\)). The experimental data used for the calculations are listed in Table 2
while the Kratky distribution functions of the aromatic core and the hydrocarbon chains as well as the corresponding integrals are plotted in Figure 6.

![Figure 6](image)

**Fig. 6.** Kratky distribution functions (2) for aromatic core \( a \) and methylene groups \( c \). \( f(y) \) denotes the fractional number of core axis \( a \) and methylene groups \( c \) pointing into the cone with angle \( y \). \( S_a \) and \( S_C \) are the corresponding order parameters, c.f. (7). \( \delta_a(y - \gamma_a) \) and \( \delta_c(y - \gamma_c) \) denote the corresponding delta distribution functions, c.f. (1).

### 3.3. Statistical Calculation of Hydrocarbon Chain Ordering

The mean dichroic rations of \( \delta_a(CH_3) \), \( \delta(CH_2) \) and \( \nu_n(CH_2) \) of hexyl chains in RO-TN-200 were calculated by means of Marčelja’s theory. The ATR-dichroic ratio in terms of the 3 components of the transition dipole moment \( M_x, M_y \) and \( M_z \) is given by

\[
R_{ATR} = \frac{E_x^2 \langle M_x^2 \rangle + E_y^2 \langle M_y^2 \rangle}{E_y^2 \langle M_y^2 \rangle}.
\]

Assuming cylindrical symmetry about the \( y \)-axis \( R_{ATR} \) is given by

\[
R_{ATR} = \frac{1}{2} \frac{E_x^2 \langle M_x^2 \rangle + E_y^2 \langle M_y^2 \rangle}{E_y^2 \langle M_y^2 \rangle}.
\]

where

\[
\langle M^2 \rangle = \frac{1}{Z} \int_0^{\pi/2} \int_0^{2\pi} \sum \int_0^{\pi} M_i^2 e^{-E_i/RT} f(y) \ dy \ d\gamma \ d\varphi
\]

is the statistical average of the squared component of the transition dipole moment (summed over all conformations). \( Z \) is the corresponding partition function and \( M_i \) the component of the transition moment corresponding to the \( i \)-th chain conformation having the potential energy \( E_i \). \( f(y) \) denotes the

* normals to the \( H-C-H \)-plane.

In case of methylene vibrations \( \delta(CH_2) \) and \( \nu_n(CH_2) \) it was assumed that

\[
M_{ij}^2 = \sum_j M_{ij}^2,
\]

where \( M_{ij} \) is the component of the transition dipole moment corresponding to the \( j \)-th methylene group in the \( i \)-th chain conformation. Summation extends over all methylene groups in the chain. The transition dipole moments considered here are assumed to be oriented in the following way:

- \( M[\delta_a(CH_3)] \) parallel to the \( C_3 \)-symmetry axis of the methyl group;
- \( M[\delta(CH_2)] \) parallel to the bisectrix of the HCH-angle;
- \( M[\nu_n(CH_2)] \) parallel to the line connecting the two corresponding H atoms.

The order parameter \( S_j \) of the \( j \)-th methylene group is defined by

\[
S_j = \frac{3}{2} \cos^2 \theta_j - \frac{1}{2},
\]

where \( \theta_j \) is the angle between the normal to the HCH plane and the director which is in our case parallel to the \( y \)-axis of the coordinate system (Figure 1). The mean order parameters \( S_c \) of the hydrocarbon chain is then defined by

\[
S_c = \frac{1}{N} \sum_{i=1}^{N} \langle S_i \rangle
\]

\[
= \frac{1}{N Z} \sum_{i=1}^{N} \int_0^{\pi} \int_0^{2\pi} \sum \int_0^{\pi} \exp \{-E_i/RT\} f(y) \ dy \ d\gamma \ d\varphi ;
\]

\( N = 5 \), number of methylene groups.

The potential energy of the chain is composed of two parts

\[
E = E_{int} + E_{ext}.
\]

\( E_{int} \) denotes the internal energy of the alkyl chain in which three successive \( \text{C}-\text{C} \) bonds can assume either trans (t), gauche + (g+) or gauche − (g−) conformation. Assuming nearest neighbour interaction between chain segments the internal energy of a \( \text{C}_n \)-chain becomes

\[
E_{int} = \sum_{i=2}^{5} \frac{3}{2} E(\xi_i, \xi_{i-1}) ,
\]

\( \xi \) stands for t, g+ or g−, respectively. The rotational barriers taken from Ref. are

\[
E(\xi, t) = 0, E(t, g^+) = \ldots
\]
Table 2. Mean values of \(R_{\text{ATR}}\); ATR dichroic ratio, c.f. (3); \(R^T\): Reduced dichroic ratio, c.f. (4), (5); \(\Theta\): Angle between transition dipole moment and long axis of the aromatic core (para-axis); \(S\): Order parameter calculated from (5); \(v\): Extension ratio of Kraatky function (2) calculated from (6); \(S\): Order parameter calculated from (7).

<table>
<thead>
<tr>
<th>Vibration Symbol</th>
<th>cm(^{-1})</th>
<th>(R_{\text{ATR}})</th>
<th>(R^T)</th>
<th>(\Theta)</th>
<th>(S)</th>
<th>(v)</th>
<th>(S)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_{\text{as}}(\text{CH}_3))</td>
<td>2930</td>
<td>1.95 (^2)</td>
<td>1.04 (\pm 0.10)</td>
<td>(\approx 90^\circ)</td>
<td>6.9</td>
<td>(-\infty)</td>
<td>1.15 - 1.00</td>
<td>0.088 - 0</td>
</tr>
<tr>
<td>(v_3(\text{CH}_2))</td>
<td>2858</td>
<td>1.92 (^2)</td>
<td>1.03 (\pm 0.10)</td>
<td>(\approx 90^\circ)</td>
<td>7.5</td>
<td>(-\infty)</td>
<td>1.14 - 1.00</td>
<td>0.082 - 0</td>
</tr>
<tr>
<td>(\delta(\text{CH}_3))</td>
<td>1465</td>
<td>2.20</td>
<td>1.18 (\pm 0.06)</td>
<td>(\approx 90^\circ)</td>
<td>4.2</td>
<td>(-\infty)</td>
<td>1.24 - 1.13</td>
<td>0.137 - 0.074</td>
</tr>
<tr>
<td>(v(\text{C} - \text{C}))</td>
<td>1114</td>
<td>1.34 (^4)</td>
<td>0.72 (\pm 0.035)</td>
<td>(\approx 35^\circ)</td>
<td>4.3</td>
<td>(-6.2)</td>
<td>1.23 - 1.18</td>
<td>0.134 - 0.097</td>
</tr>
<tr>
<td>(v(\text{C} = \text{N}))</td>
<td>2222</td>
<td>0.48</td>
<td>0.257 (\pm 0.005)</td>
<td>(0^\circ)</td>
<td>0.68 - 0.72</td>
<td>2.2 - 2.25</td>
<td>0.495 - 0.480</td>
<td>(\text{aromatic core})</td>
</tr>
<tr>
<td>(v(\text{C} = \text{N}))</td>
<td>1630</td>
<td>0.70</td>
<td>0.374</td>
<td>(22^\circ) (^5)</td>
<td>0.68 - 0.72</td>
<td>2.2 - 2.25</td>
<td>0.495 - 0.480</td>
<td>(S = 0.48)</td>
</tr>
</tbody>
</table>

\(^1\) Calculated from \(R_{\text{ATR}}\) by means of (4). \(E_{xz}^2/E_{yz}^2 + E_{xz}^2/E_{yz}^2 = 1.87\) was calculated following Reference \(^{12}\). The refractive indices of RTN-200 are: \(n'' = 1.82\) and \(n' = 1.55\) respectively.

\(^2\) Estimated values. No band shape analysis was performed.

\(^3\) In order to minimize steric hinderance mean orientation of the hydrocarbon chains was assumed parallel to the para-axis.

\(^4\) Determined by means of band shape analysis, \(\Delta v_{13} = 6.5\) cm\(^{-1}\). The second band was found to be at 1108 cm\(^{-1}\) with \(E_{xz}^2/E_{yz}^2 = 1.87\) (c.f. (8)). \(R_{\text{ATR}}\) was calculated from (8).

\(^5\) Calculated angle between the transition moment of \(v(\text{C} = \text{N})\) and the para-axis by means of Equation (5).

\[ E_{\text{ext}}(g^z, g^z) = 400\ \text{cal/mol}\] and \[ E_{\text{ext}}(g^z, g^z) = 2200\ \text{cal/mol}. \]

\(E_{\text{ext}}\) denotes the energy of the chain in the mean molecular field of the nematic phase. In analogy to Ref. \(^4\) \(E_{\text{ext}}\) becomes

\[ E_{\text{ext}} = - (2 C_\alpha S_c V_{\text{cc}} + C_\alpha S_a V_{\text{ca}}) \sum_{i=1}^{n} S_i. \quad (10) \]

The subscripts \(a\) and \(c\) stand for aromatic rings and chains, respectively, \(C_\alpha\) and \(C_c\) are the corresponding volume fractions, \(S_a\) and \(S_c\) denote the mean order parameters. For 4-(4′-n-hexyl-benzylidene amino)benzonitrile the volume fractions as estimated from a molecular model were taken as \(C_c = 0.36\) and \(C_a = 0.64\), respectively. \(S_a\) is 0.48 according to Table 2. The constant \(V_{\text{cc}}\) describing the energy of a chain segment in the field of the other chains is estimated to be 680 cal/mol. \(V_{\text{ca}}\) denotes the energy of a chain segment in the field of the aromatic cores, it is the only adjustable parameter in Markelja's theory. The factor 2 is included to normalize the values of \(S_c\) between zero and one for the disordered and the all-trans ordered state, respectively.

The values of the order parameters \(S_i, S_a, S_c\) and of the dichroic ratio \(R_{\text{ATR}}\) of the three group vibrations may now be obtained as self consistent solutions of Eqs. (8), (9) and (10). The results of our calculations are summarized in Table 3.

Table 3. Values of order parameters \(S_i\), mean order parameter \(S_c\) of hydrocarbon chains and ATR dichroic ratios calculated for different constants \(V_{\text{cc}}\) and \(V_{\text{ca}}\) at \(T=8^\circ\)C.

<table>
<thead>
<tr>
<th>(V_{\text{cc}}) (cal/mol)</th>
<th>680</th>
<th>680</th>
<th>680</th>
<th>400</th>
<th>200</th>
<th>50</th>
<th>50</th>
<th>680</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>(V_{\text{ca}}) (cal/mol)</td>
<td>500</td>
<td>100</td>
<td>50</td>
<td>0</td>
<td>50</td>
<td>50</td>
<td>50</td>
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</tr>
<tr>
<td>(S_1)</td>
<td>0.456</td>
<td>0.311</td>
<td>0.293</td>
<td>0.270</td>
<td>0.260</td>
<td>0.254</td>
<td>0.276</td>
<td>0.243</td>
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<tr>
<td>(S_2)</td>
<td>0.385</td>
<td>0.145</td>
<td>0.115</td>
<td>0.077</td>
<td>0.059</td>
<td>0.049</td>
<td>0.086</td>
<td>0.032</td>
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<tr>
<td>(S_3)</td>
<td>0.394</td>
<td>0.150</td>
<td>0.119</td>
<td>0.080</td>
<td>0.062</td>
<td>0.052</td>
<td>0.089</td>
<td>0.034</td>
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<tr>
<td>(S_4)</td>
<td>0.343</td>
<td>0.094</td>
<td>0.064</td>
<td>0.026</td>
<td>0.009</td>
<td>0.000</td>
<td>0.035</td>
<td>0.018</td>
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<tr>
<td>(S_5)</td>
<td>0.304</td>
<td>0.113</td>
<td>0.090</td>
<td>0.060</td>
<td>0.046</td>
<td>0.039</td>
<td>0.067</td>
<td>0.025</td>
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<tr>
<td>(S_c)</td>
<td>0.376</td>
<td>0.163</td>
<td>0.136</td>
<td>0.103</td>
<td>0.087</td>
<td>0.079</td>
<td>0.111</td>
<td>0.063</td>
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<tr>
<td>(R_{\text{ATR}}(\delta(\text{CH}_3))) (^2)</td>
<td>2.76</td>
<td>2.09</td>
<td>2.02</td>
<td>1.95</td>
<td>1.92</td>
<td>1.90</td>
<td>1.96</td>
<td>1.87</td>
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<tr>
<td>(R_{\text{ATR}}(v_{\text{as}}(\text{CH}_3)))</td>
<td>4.82</td>
<td>2.83</td>
<td>2.67</td>
<td>2.48</td>
<td>2.39</td>
<td>2.36</td>
<td>2.53</td>
<td>2.27</td>
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<tr>
<td>(R_{\text{ATR}}(\delta(\text{CH}_3)))</td>
<td>2.37</td>
<td>2.53</td>
<td>2.55</td>
<td>2.57</td>
<td>2.58</td>
<td>2.58</td>
<td>2.56</td>
<td>2.59</td>
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</tr>
</tbody>
</table>

\(^1\) For a detailed description of the applied procedure leading to these results the reader is referred to Reference \(^{25}\).

\(^2\) The ratio of the ATR electric field components \((E_{xz}^2 + E_{yz}^2)/E_{yz}^2 = 1.87\) involved in \(R_{\text{ATR}}\) [c.f. (8)] was calculated from Harrick \(^{12}\).
4. Remarks and Conclusions

4.1. Boundary Layer

The mean penetration depth \( d_p \) of IR-ATR light into the liquid crystal is calculated\(^2\) to be \( d_p = 0.42 \) to 1.41 microns in the wavelength range \( \lambda = 3 \) to 10 microns for an angle of incidence \( \Theta_{\text{ATR}} = 30^\circ \) and a ratio of refractive indices \( \tilde{n}_{\text{LC}}/n_{\text{Ge}} = 0.413 \). \( \tilde{n}_{\text{LC}} \) = average refractive index of liquid crystal, \( n_{\text{Ge}} \) = refractive index of germanium. The spectra depicted in Sect. 3 are therefore related to a thin boundary layer of liquid crystal molecules at the germanium-liquid crystal interface.

4.2. Polarization of Absorption Bands

The assignment of infrared absorption bands of benzalaniline (which is identical with the aromatic core of RO-TN-200) is reported\(^{15}\) in a previous infrared study on liquid crystals. Number and intensity of absorption bands with polarization parallel and perpendicular to the molecular axis are about the same\(^{15}\). However, in our spectra (Figs. 3, 4) it is found that practically all intense absorption bands belong to vibrations polarized more or less parallel to the para-axis. This may be due to the strong dielectric anisotropy \( \Delta \varepsilon = \varepsilon_\parallel - \varepsilon_\perp = +18.3 \) of RO-TN-200\(^{19}\) compared with \( \Delta \varepsilon < 0 \) of benzalaniline.

4.3. Overlapping of Absorption Bands

In order to determine the dichroic ratio \( R_{\text{ATR}} \) it is necessary to know the integral- or the peak absorption coefficients\(^{20}\) along both polarizations, parallel and perpendicular, respectively. Since many absorption bands of interest are overlapped by other bands, line shape analysis is a prerequisite for an accurate determination of the dichroic ratio.

Line shape analysis was carried out to determine the dichroic ratio of the \( 1114 \) cm\(^{-1}\) absorption band (Fig. 3) which could be assigned to \( \nu(C - C) \), c.f. Table 1 and 2. The dichroic ratio of the second band in the doublet (Fig. 3) was determined to be \( R_{\text{ATR}} = 5.3 \), with \( \Delta \alpha_{1/2} = 2.5 \) cm\(^{-1}\). Therefore, it must be assigned to a vibration of the aromatic core which is perpendicular polarized with respect to the long molecular axis. Line shape analysis in the region of \( \delta_s(CH_3) \) and \( \delta(CH_2) \) is not necessarily required because the dichroic ratios of the overlapping bands \( [\text{e.g. } \delta_s(CH_3) \text{ at } 1456 \text{ cm}^{-1}] \) are approximately the same as those of the bands of interest.

4.4. Comparison of Calculated an Experimentally Determined Dichroic Ratios

In Table 3 (bottom) the mean dichroic ratios of typical hydrocarbon chain vibrations are listed as a function of the molecular field coupling constants \( V_{\text{ee}} \) and \( V_{\text{ea}} \). The set \( V_{\text{ee}} = 680 \text{ cal/mol} \) and \( V_{\text{ea}} = 472 \text{ cal/mol} \) (left) was used by Marčelja\(^{4}\). The case for no coupling \( V_{\text{ee}} = V_{\text{ea}} = 0 \) is listed on the right hand side. Comparing Table 3 with Table 2 and Fig. 6 leads to the conclusion that \( V_{\text{ea}} \) must be expected to be about 10 times smaller than proposed in Ref.\(^{4}\) to get a value for the mean order parameter which is in satisfactory agreement with the experimentally determined \( S_e = 0.11 \). This result is in agreement with recent theoretical considerations\(^{21}\). In addition to the above the coupling constant \( V_{\text{ee}} \) turned out to be rather unspecific.

There still remains a discrepancy between the calculated and experimentally determined dichroic ratios, especially so with respect to the symmetric methyl bending vibration \( \delta_s(CH_3) \), see Table 2 and 3. From the calculated values of \( R_{\text{ATR}}(\delta_s(CH_3)) \) it must be concluded that the transition moment of \( \delta_s(CH_3) \), expected to lie parallel to the direction of the last \( C - C \)-bond, exhibits a significant polarization perpendicular to the para-axis. However, the experimental value of \( R_{\text{ATR}}(\delta_s(CH_3)) \) results in a slight polarization parallel to the molecular axis. A plausible explanation for this discrepancy could be steric hinderance which is expected to become significant for molecules in the liquid crystalline environment-whereas the calculated data in Table 3 are derived from the isolated molecule.

Finally it should be mentioned that \( R_{\text{ATR}}(\delta_s(CH_3)) \) of the hexyl component is somewhat higher than the experimentally determined value in Table 2. This is due to RO-TN-200 containing \( 33\% \) n-propyl Schiff base whose methyl group exhibits a higher order parameter than that of the hexyl component (c.f. Sec. 3.2.2). The experimentally determined dichroic ratio will nevertheless remain significantly lower than the calculated ratio.

4.5. Application of Molecular Field Theory to Biological Systems

Based on his liquid crystal results\(^4\) Marčelja extended his theory to calculate the conformation of hydrocarbon chains in oriented lipid bilayers and to determine the pressure-area diagrams of spread
monolayers. His theory was also used to determine hydrocarbon chain conformations in systems of lipid multilayers as well as to study the influence of proteins on the conformation of the hydrocarbon chains of surrounding lipids.

Although very good agreement between calculated and experimental results is reported in Refs. it should be recognized that Marcelja's theory is not fully consistent in view of our experimental findings as well as of those published recently by others. Marcelja's theory reproduces correctly the even odd effect of transition temperature, transition entropie and core-order parameters of a homologous serie of liquid crystals, however, it can not correctly reproduce order parameters and dichroic ratios of hydrocarbon chains when using the same set of parameter as for the core-order calculations.

Acknowledgement

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