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Molecular Biaxiality in Nematic Liquid Crystals as Studied by Infrared Dichroism

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The order parameter S_{zz} and the molecular biaxiality parameter $D = S_{xx} - S_{yy}$ have been evaluated for various nematic liquid crystal materials employing infrared dichroism measurements. The influence of the terminal group, the ring systems and an ester linkage group on S_{zz} and D has been studied for various terminally polar and terminally non-polar liquid crystal materials. Our experimental results for the cyanobiphenyl CB5 are in agreement with NMR-studies, if we allow for a small local field correction which is nearly within our experimental measuring accuracy. For the first time, the order parameters S_{xx} , S_{yy} and S_{zz} of heptyl-cyanophenyl-cyclohexan (PCH7) are determined independently by analyzing 3 different benzene ring skeleton vibrations. The existence of a weakly pronounced molecular biaxiality is demonstrated for most of the liquid crystal materials investigated. Moreover the variation of D as a function of S_{zz} is found to be approximately of the form predicted by the molecular field theory.

INTRODUCTION

The orientational ordering of nematic liquid crystals is, by restriction on tensors of second rank, generally to be described by an ordering matrix S_{ij} where $i, j = x, y, z$ denote orthogonal, but otherwise arbitrary molecular axes. Taking into account the macroscopic symmetries of the nematic phase (optically uniaxial, apolar), S_{ij} still possesses five independent elements. Only if the directions of the molecular principal axes are known, can S_{ij} be diagonalized, having two independent diagonal elements. If, in addition, cylindrical symmetry about the long molecular z -axis is assumed, $S_{xx} = S_{yy} = -S_{zz}/2$ results, and the orientational order is completely determined by only one order parameter. As the symmetry of the molecules in general is low, neither are the directions of the principal axes exactly known nor is the cylindrical symmetry of the molecules realized. Moreover it is experimentally extremely difficult to obtain complete information about the matrix S_{ij} for customary liquid crystal molecules. This problem is circumvented by approximating the molecules by cylindrical rods. Assuming a much higher symmetry of the molecules than they really have, the orientational ordering is characterized by only one order parameter, usually S_{zz} . On the other hand, nuclear magnetic resonance investigations on PAA¹ and CB5-d₁₅² have indeed demonstrated that the rotational symmetry about the long molecular axis is not fulfilled and the orientational order must

be described by two order parameters S_{zz} and $D = S_{xx} - S_{yy}$. D characterizes the deviation from the molecular rotational symmetry and is called molecular biaxiality. There is a strong interest of theoreticians concerning the consequences of molecular biaxiality.³⁻¹⁰ Already, in 1975, Luckhurst *et al.*⁷ had developed a molecular field theory taking into account the deviation from molecular cylindrical symmetry. Due to the lack of sufficient experimental data for the order parameter D , a comparison with this theory was, until recently, only partially possible, mainly because D could be determined only by sophisticated NMR-techniques.

In principle, the desired information about the other parameters S_{zz} and D can also be obtained by an optical method by analyzing the dichroism of two distinctly separated absorption bands, if the orientations of the related transition moments are different and precisely known and the unknown local field correction can be neglected.¹¹⁻¹⁶

In a number of publications the molecular biaxiality of *guest* molecules in liquid crystal hosts has been evaluated by NMR- and optical investigations.^{13,14,17,18}

This paper gives for the first time a report of measurements of the order parameters S_{zz} and D on *pure* nematics employing the *infrared dichroism method* on selected characteristic vibrational modes of the liquid crystal molecules. In order to estimate the influence of the local electric field correction on our measured order parameters S_{zz} and D , we first compare our results for CB5 with the NMR-studies of Emsley *et al.*² for CB5-d₁₅. Secondly we determine S_{xx} , S_{yy} and S_{zz} for PCH7 independently by analysing the IR-dichroism of three vibrational bands whose transition moments are orthogonal to each other. This allows us for the first time to check experimentally the consistency with the mathematical requirement that $S_{xx} + S_{yy} + S_{zz} = 0$. Furthermore, we investigate how a local field correction influences this equation. Afterwards the influence of the molecular structure on the order parameters S_{zz} and $D = S_{xx} - S_{yy}$ will be reported. Finally a comparison of our data with the molecular field theory of Luckhurst *et al.*⁷ will be presented.

THEORY

The orientation of a particular molecule with the cartesian molecular axes (x, y, z) relative to the laboratory axes (U, V, W) is determined by specification of the Euler angles ϕ, θ, ψ (see Figure 1). The angles (α, β) specify the direction of the transition moment M in the molecular frame. Assuming at least C_{2v} -symmetry of the molecules, the symmetry axes define the principal axes of the molecules. By choosing these directions parallel to the axes (x, y, z) the ordering matrix S_{ij} , as introduced by Saupe,¹⁹ is diagonal. Instead of S_{xx} , S_{yy} and S_{zz} , it is more convenient to use the two independent order parameters S_{zz} and D as given by

$$\begin{aligned} S_{zz} &= \langle 1/2 (3 \cos^2\theta - 1) \rangle \\ D &= S_{xx} - S_{yy} = \langle 3/2 \sin^2\theta \cos 2\psi \rangle \end{aligned} \quad (1)$$

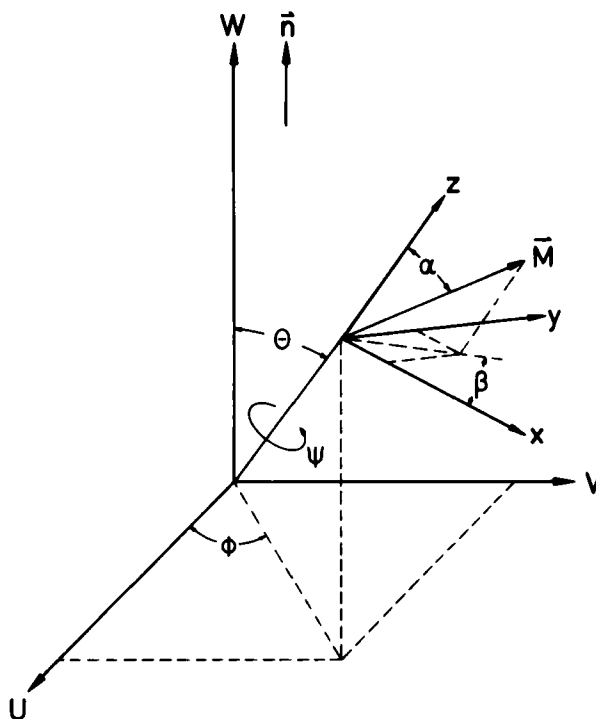


FIGURE 1 Orientation of the transition moment \vec{M} in the molecular cartesian coordinate system and definition of the molecular axes x, y, z relative to the laboratory axes U, V, W .

where the brackets denote the statistical average taken over all molecules. As usual the order parameter S_{zz} characterizes the long range orientational order of the long molecular principal axis z . The order parameter D represents a quantitative measure of the deviation from molecular rotational symmetry about the z -axis and for $D \neq 0$, the molecules show molecular biaxiality. This means that there is a different tendency of the two short principal axes x and y to align parallel to the director axis \hat{n} . The orientational distribution function then does not only depend on θ , but also on ψ . This does not at all imply that the sample is macroscopically biaxial. That would only happen if the different degree of alignment of the x and y -axis does not only exist for single molecules, but is correlated between different molecules. For molecules with C_{2v} symmetry, the order parameters S_{zz} and D are related to the optical order parameter S_{op} by:

$$S_{op} = \frac{R_{ob} - 1}{R_{ob} + 2} = S_{zz} (1 - 3/2 \sin^2 \alpha) + \frac{D}{2} \sin^2 \alpha \cdot \cos 2\beta \quad (2)$$

where $R_{ob} = A_{\parallel}/A_{\perp}$ is the measured dichroic ratio, and A_{\parallel} and A_{\perp} are the absorbances of the investigated transition with light polarization parallel and perpendicular to the nematic director \hat{n} . The difference of Equation (2) to the equivalent expres-

sion given in Reference 13 is due to a slightly different definition of D in accordance with References 2 and 7. Usually $D = 0$ is assumed and Equation (2) then reduces to the familiar equation first derived by Saupe.¹² If the transition moment is parallel to the z -axis, $\alpha = 0$ holds and deviations from the molecular rotational symmetry cannot be detected by an optical method. In order to determine S_{zz} and D from Equation (2), two absorption bands with different directions of the transition moments are needed. We consider two absorption bands with respective directions of the transition moments parallel to the y -axis ($\alpha_1 = 90^\circ$, $\beta_1 = 90^\circ$) and parallel to the z -axis ($\alpha_2 = 0^\circ$, $\beta_2 = 0^\circ$).

The ratio of the optical order parameters $S_{\text{op},yy}/S_{\text{op},zz}$ is then given with equation (2) by:

$$\frac{S_{\text{op},yy}}{S_{\text{op},zz}} = -\frac{1}{2} \left(1 + \frac{D}{S_{zz}} \right) \quad (3)$$

If the two different transition moments are directed parallel to the x -axis and to the y -axis respectively, an analogous ratio of the order parameters can be written:

$$\frac{S_{\text{op},xx}}{S_{\text{op},yy}} = \frac{1 - \frac{D}{S_{zz}}}{1 + \frac{D}{S_{zz}}} \quad (4)$$

The ratios $S_{\text{op},yy}/S_{\text{op},zz}$ in Equation (3) and $S_{\text{op},xx}/S_{\text{op},yy}$ in Equation (4) will be temperature dependent only if D is non-zero. But this argument is not reversible. If the ratio in Equation (3) and (4) is independent of temperature then $D = 0$ need not be true because the temperature dependencies of D and S_{zz} could compensate each other. It must further be emphasized that $D \neq 0$ can only be concluded from a temperature dependence of $S_{\text{op},yy}/S_{\text{op},zz}$ or $S_{\text{op},xx}/S_{\text{op},yy}$ if the local field correction may be neglected. Taking into account the local field correction, the dichroic ratio R_{ob} in Equation (2) has to be replaced¹² by $R = g \cdot R_{\text{ob}}$:

$$R = \frac{n_{\parallel}}{n_{\perp}} \left(\frac{g_{\perp}}{g_{\parallel}} \right)^2 \frac{A_{\parallel}}{A_{\perp}} = g \cdot R_{\text{ob}} \text{ with } g = \frac{n_{\parallel}}{n_{\perp}} \left(\frac{g_{\perp}}{g_{\parallel}} \right)^2 \quad (5)$$

Here n_{\parallel} and n_{\perp} are the refractive indices and g_{\parallel} and g_{\perp} the internal electric field factors for light polarization parallel and perpendicular to the optical axis. Assuming $g > 1$ and an absorption band with positive dichroism, it follows that $R > R_{\text{ob}}$. If $g < 1$ holds, the relation is inverted. As Equation (4) uses two absorption bands with $R = R_x < 1$ and $R = R_y < 1$, the influence of a local field correction is minimized in contrast to Equation (3) where two bands with $R = R_z > 1$ and $R = R_y < 1$ are utilized. If an isotropic local field is assumed $g_{\parallel} = g_{\perp}$ is valid and this results in the familiar Vuks correction factor $g = n_{\parallel}/n_{\perp}$.²⁰

Various approximate models for the local electric field have been proposed and the corresponding correction factors g have been calculated. As an exact solution of the local field problem is out of sight, we have made an experimental approach.

EXPERIMENTAL

A reproducible homogeneous planar orientation of the molecules was achieved by oblique evaporation of SiO at an angle of 50° to the normal to the sodium chloride plates. The cells were spaced with 4–8 μm thick mylar strips and variations in thickness across the cell were minimized by adjusting pressure on the sodium chloride plates to produce the minimum number of interference fringes. The cells were filled by capillary action and the quality of the alignment was controlled by microscopic observation. Only homogeneously oriented samples were used for our investigations. The measurements were performed using a Perkin-Elmer 580 B double beam spectrophotometer equipped with a double chopper system to eliminate the temperature dependent emission radiation of the sample. A wire grid polarizer with an efficiency of 98.8% at 2240 cm^{-1} and 99.21% at 800 cm^{-1} was used. The measured dichroic ratios were corrected for the imperfections of the polarizer by the method of Reference 21. The optical axis of the sample was oriented at 45° (or -45°) to the slit direction of the measuring instrument to remove the instrument polarization.²¹ By aligning the polarizer parallel to the optical axis of the sample, the absorbance A_{\parallel} was obtained. After rotating the polarizer by 90° , A_{\perp} was recorded. In order to gain the maximum measuring precision of the spectrophotometer, the cell thickness was adjusted such that $A_{\parallel} < 1.5$ and $A_{\perp} > 0.1$ is fulfilled. Instead of the integrated absorption values we took the absorption values A_{\parallel} and A_{\perp} at the peak absorption wavelength. With a typical band half-width of 10 cm^{-1} and a spectral resolution of 2.3 cm^{-1} , a further correction of the absorption values is not necessary.²² To optimize our signal/noise ratio, we scanned only over the interesting absorption wavelength range with the slowest possible scan speed. As we always observed a small, long time dependent drift of the zero % transmission line, we always measured additionally the true zero % transmission line for the respective wavelength region. Further the available digital peak absorption values were used instead of the data recorded by the chart recorder. With all these procedures we have considerably improved the precision of the infrared dichroism method. The reproducibility of the order parameter S_{zz} with different measuring cells was better than 0.015.

We carried out dichroism investigations on 4-n-pentyl-4'-cyanobiphenyl (5 CB, N 34.6 I), on 4-n-heptyl-1-(4'-cyanophenyl)cyclohexane (PCH7, N 57.25 I) and on the various liquid crystal substance classes given in Figure 2. The order parameters S_{zz} were determined from the dichroism of the $\text{C}\equiv\text{N}$ stretching vibration at 2230 cm^{-1} and/or the benzene ring $\text{C}=\text{C}$ skeleton vibrations (" 1606 cm^{-1} ", " $1520\text{--}1480\text{ cm}^{-1}$ ", " 1011 cm^{-1} ", see Figure 3). All these vibrational modes are localized in the rigid central core of the molecules, represent strong, well localized, characteristic group vibrations, are mostly free from overlapping bands, and are therefore ideally suited for order parameter determinations. The transition moments point parallel to the $\text{C}\equiv\text{N}$ connection axis and to the *para*-axis of the benzene ring respectively. Both directions represent symmetry axes of the benzonitrile group or the benzene ring, possessing at least local C_{2v} symmetry. Assuming that both axes are parallel, we denoted the common axis as the z-axis. The y-axis of the molecular coordinate system stands perpendicular to the benzene ring plane. By analysing the dichroism

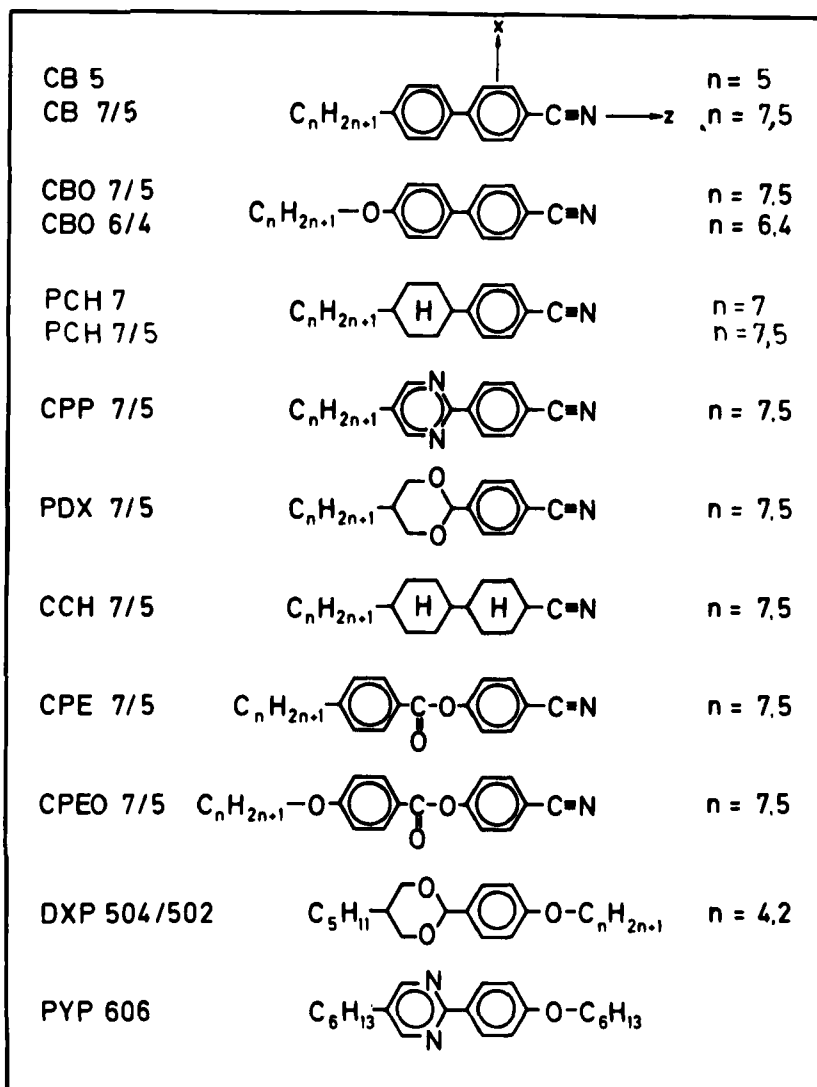


FIGURE 2 Nematic liquid crystal substances and molecular coordinate axes x, y, z . The y -axis stands perpendicularly to the plane of the benzene ring. If the liquid crystal molecule possesses two benzene rings which are not coplanar, the y -direction is chosen perpendicular to the angle-bisecting plane of the two aromatic rings. The pentyl (butyl) and heptyl (hexyl)-components in the binary mixtures were always in molar proportions of 40%:60%.

of the collective C-H-out-of-plane vibration of the benzene ring ("900-650" cm^{-1} , transition moment parallel to the y -axis,²³ see Figure 3), the order parameters S_{yy} and D were obtained.

A remark should be made about the selection of these materials. Terminally polar as well as terminally non-polar representatives are considered. Much information about material properties such as elastic constants, viscosities and dielectric constants has been collected for these materials by the work of Schadt²⁴ and Scheu-

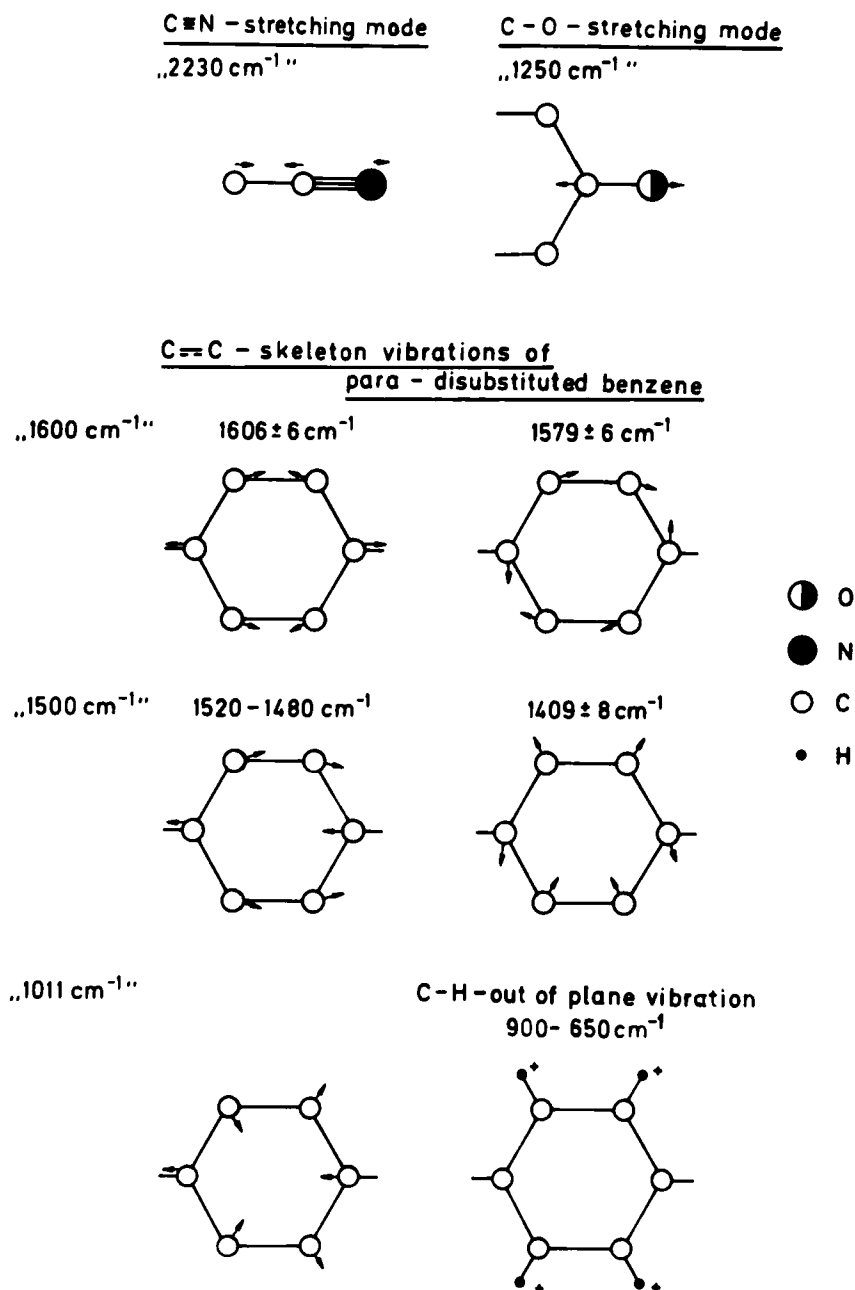


FIGURE 3 Benzene ring skeletal vibrations.²³ The vibration frequencies depend slightly upon the *para*-substituents. The (+)-sign means that the hydrogen atoms move perpendicularly to the drawing plane.

ble.²⁵ In order to include also substance classes possessing only a monotropic phase and to broaden the nematic phase ranges, the authors have chosen mostly binary mixtures. Directed by the intention to explore relations between order parameters and material properties we have also taken binary mixtures with the same mixture ratio as has been used in References 24 and 25.

Further, this paper forms the basis for studies of correlations between order parameters of dichroic dyes and liquid crystal hosts in guest host systems. The corresponding results will be presented in a different paper. The IR-technique averages over the order parameters of the two different homologues as their corresponding absorption bands coincide and one has no chance to separate the order parameters of the two single components. The comparison of CB5 with CB7/5 and PCH7 with PCH7/5 presented later on let us realize that the difference of the order parameters S_{zz} and D between the heptyl- and pentyl-homologues must be small and about of the same magnitude as the measuring error. Taking into account all these points of view, we think that the usage of the binary mixtures given in Figure 2 represents no serious disadvantage. But it should be mentioned here that order parameters S_{zz} of single components in multicomponent mixtures can be determined by the dichroism method only if the single components possess characteristic vibrations showing well separated absorption bands. Such an experiment has been accomplished recently with a three component mixture.²⁶ In this connection, the infrared dichroism method could become a very powerful method for investigating order parameters of single components in mixtures by using differently deuteriated components.

An additional problem arises if a molecule contains two benzene rings which are not coplanar (CB5, CB7/5, CB06/4, CB07/5) and the absorption bands of the two benzene rings are not resolved spectroscopically. In that case, we choose the y -direction perpendicular to the angle-bisecting plane of the two aromatic rings. Assuming an angle of 32° between the two benzene ring planes, as has been determined by a NMR-study on CB5,²⁷ our S_{zz} and D -values represent averages over both ring systems (see Appendix).

RESULTS AND DISCUSSION

1. Estimation of the influence of the local field correction

1.1 Order parameters S_{zz} and D of cyanopentylbiphenyl (CB5) For this purpose a comparison of the order parameters S_{zz} and D of cyanopentylbiphenyl (CB5) as determined by proton-(deuterium) NMR (Emsley *et al.*²) and IR-dichroism (our data) was performed and is given in Figure 4a and Figure 4b as a function of the reduced temperature. The S_{zz} -values as evaluated from Equation (5) with $g = 1$ are systematically slightly lower than the values given from the NMR-investigation. Taking into account our measurement uncertainty of $\pm \begin{smallmatrix} 0.010 \\ 0.005 \end{smallmatrix}$ in S_{zz} , the discrepancy between the order parameter from the 1496 cm^{-1} band and the NMR-result is very small. A satisfactory agreement between NMR- and IR-dichroism data is observed for the order parameter D as depicted in Figure 4b. A remark has to be

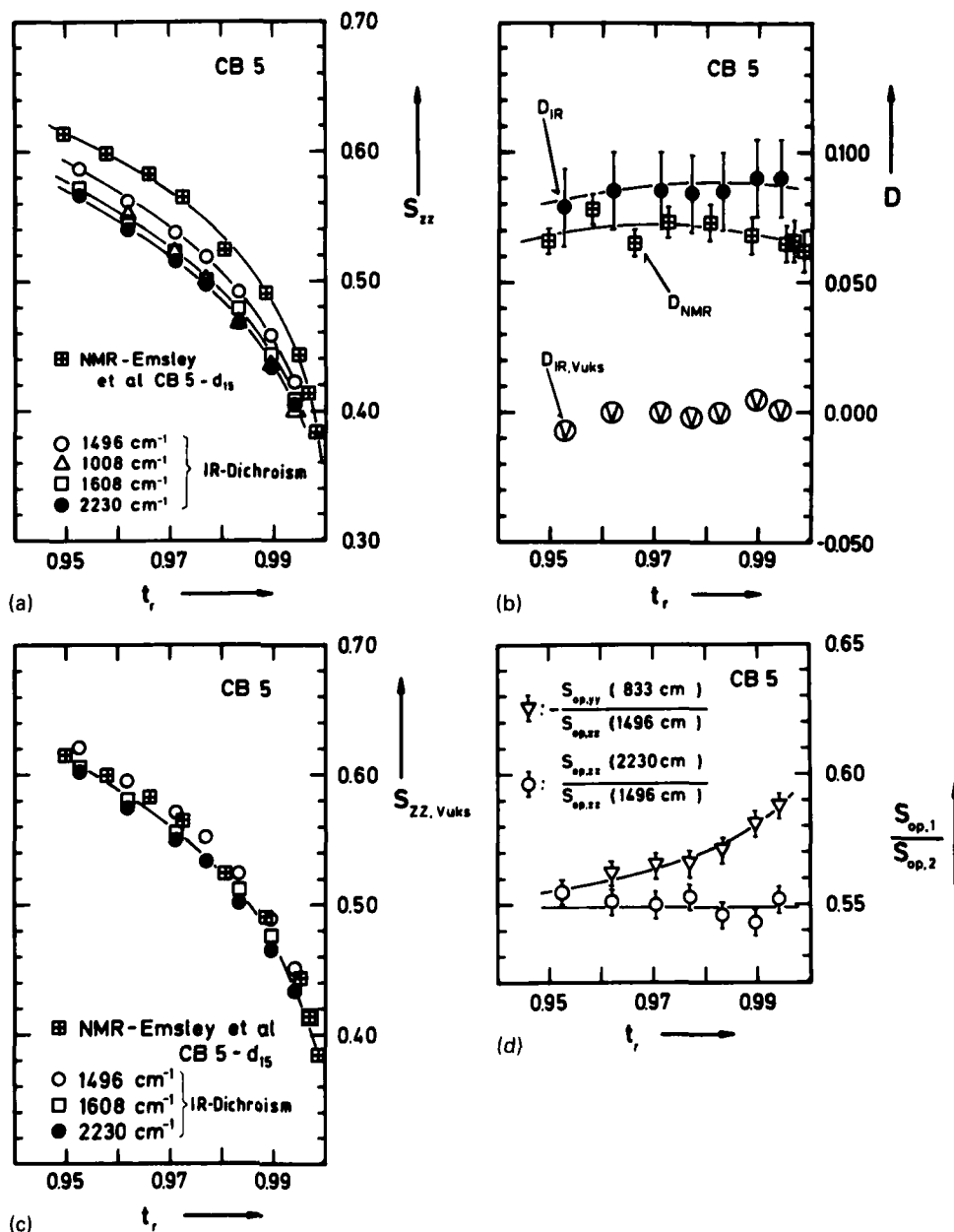


FIGURE 4 Order parameter data for CB5 as a function of reduced temperature $t_r = T/T_c$ (T_c = nematic-isotropic transition temperature) from the NMR-study of Emsley² and from our IR-dichroism studies; (a) S_{zz} of CB5- d_{15} by Emsley (\boxplus), S_{zz} from IR-dichroism of absorption bands at 1496 cm^{-1} (\circ), 1008 cm^{-1} (\triangle), 1608 cm^{-1} (\square) and 2230 cm^{-1} (\bullet); (b) D_{NMR} of CB5- d_{15} by Emsley (\boxplus), D_{IR} from IR-dichroism of 1496 cm^{-1} and 833 cm^{-1} absorption bands (\bullet), $D_{\text{IR,Vuks}}$ corrected by the Vuks field factor $g_v = n_{\parallel}/n_{\perp}$ (see Equation 5 and Reference 20) using refractive indices measured at $\lambda = 0.633 \text{ } \mu\text{m}$ (\odot); (c) S_{zz} of CB5- d_{15} by Emsley (\boxplus), $S_{zz,Vuks}$ from IR-dichroism of the absorption bands at 1494 cm^{-1} (\circ), 1606 cm^{-1} (\square) and 2230 cm^{-1} (\bullet) corrected by the Vuks field factor g_v ; (d) Ratio $-S_{op,yy}(833 \text{ cm}^{-1})/S_{op,zz}(1496 \text{ cm}^{-1})$ and $S_{op,zz}(2230 \text{ cm}^{-1})/S_{op,zz}(1496 \text{ cm}^{-1})$ of CB5 as a function of t_r . The latter ratio was normalized at $t_r = 0.9525$ to the value of the former ratio.

made about the evaluation of D_{NMR} in Reference 2. Emsley determined the local ordering of the protonated ring of CB5-d₁₅ presuming an effective C_{2v} symmetry of the whole CB5-d₁₅ molecule. He assumed that the second phenyl ring connected with the alkyl chain changes between four energy equivalent positions generated by hindered rotation about z . We can follow Emsley's presumption assuming the two benzene rings to be coplanar on the time average. In that case our D_{IR} -values are about 17% smaller and the correspondence with the NMR-data would be only better.

In order to look for the influence of the local field, we applied the correction from Vuks²⁰ with $g_v = n_{\parallel}/n_{\perp} > 1$. The refractive indices n_{\parallel}, n_{\perp} were determined at $\lambda = 0.633 \mu\text{m}$ using an Abbé refractometer. The dispersion dependence of n_{\parallel} and n_{\perp} was neglected, because we are mainly interested in observing the qualitative trends of any correction with $g \neq 1$. Figure 4c shows that the agreement between the NMR- and IR-dichroism data for the order parameter S_{zz} is more satisfactory if the Vuks correction is applied. On the other hand this is not true as far as the order parameter D is concerned. As shown in Figure 4b, we observe $D_{\text{IR, Vuks}} = 0$ in contradiction to the NMR-result. In summary, we can ascertain that the order parameters S_{zz} and D determined by IR-dichroism are in satisfactory correspondence with the NMR-data if we allow for a small local field correction with $1 < g < g_v$, which is almost within our measuring accuracy and therefore can be neglected. There may incidentally be other explanations of the small discrepancy between S_{zz} (1496 cm⁻¹) and S_{zz} (NMR). Firstly Emsley's CB5-sample showed a 0.5° higher clearing point and therefore had possibly been of higher purity. Secondly an influence of the deuteration on the order parameter cannot be completely excluded.²⁸

It should be commented that the differences in the S_{zz} -values determined with the various absorption bands do not present a difficulty, because the transition moment directions do not have to point exactly in the same direction. Our results for CB5 are completed in Figure 4d where the temperature dependencies of the ratios— $S_{\text{op,yy}} (833 \text{ cm}^{-1}) / (S_{\text{op,zz}} (1496 \text{ cm}^{-1}))$ and $S_{\text{op,zz}} (2230 \text{ cm}^{-1}) / S_{\text{op,zz}} (1496 \text{ cm}^{-1})$ are depicted. As expected, the latter ratio is temperature independent. The former ratio reveals a considerable deviation from the value + 0.5 (look for comparison at Equation (3)) and a distinct temperature dependence. If the local field correction is negligible, this result is in accordance with $D \neq 0$.

A remark should be made about the infrared measurements on CB5 published recently by Aver'yanov *et al.*²⁹ Applying the isotropic field correction ($g = g_v$), they measured, with an homogeneous planar cell, a much lower order parameter $S_{zz, \text{Vuks}}$ than Emsley from his NMR-experiment.² They proposed a field correction with $g > g_v$. This directly contradicts our results given in Figures 4a and 4c, because we determined a satisfactory correspondence between the S_{zz} and S_{zz} -values from the NMR-study for $1 < g < g_v$. As our S_{zz} -values are considerably larger than the S_{zz} -values of Aver'yanov *et al.* one must presume that their liquid crystal layer was not perfectly aligned.

1.2 Ordering matrix S_{ij} of 4-heptyl-1-(4'-cyanophenyl)cyclohexane (PCH7) We have selected PCH7 for different reasons. First with the Raman Scattering method,

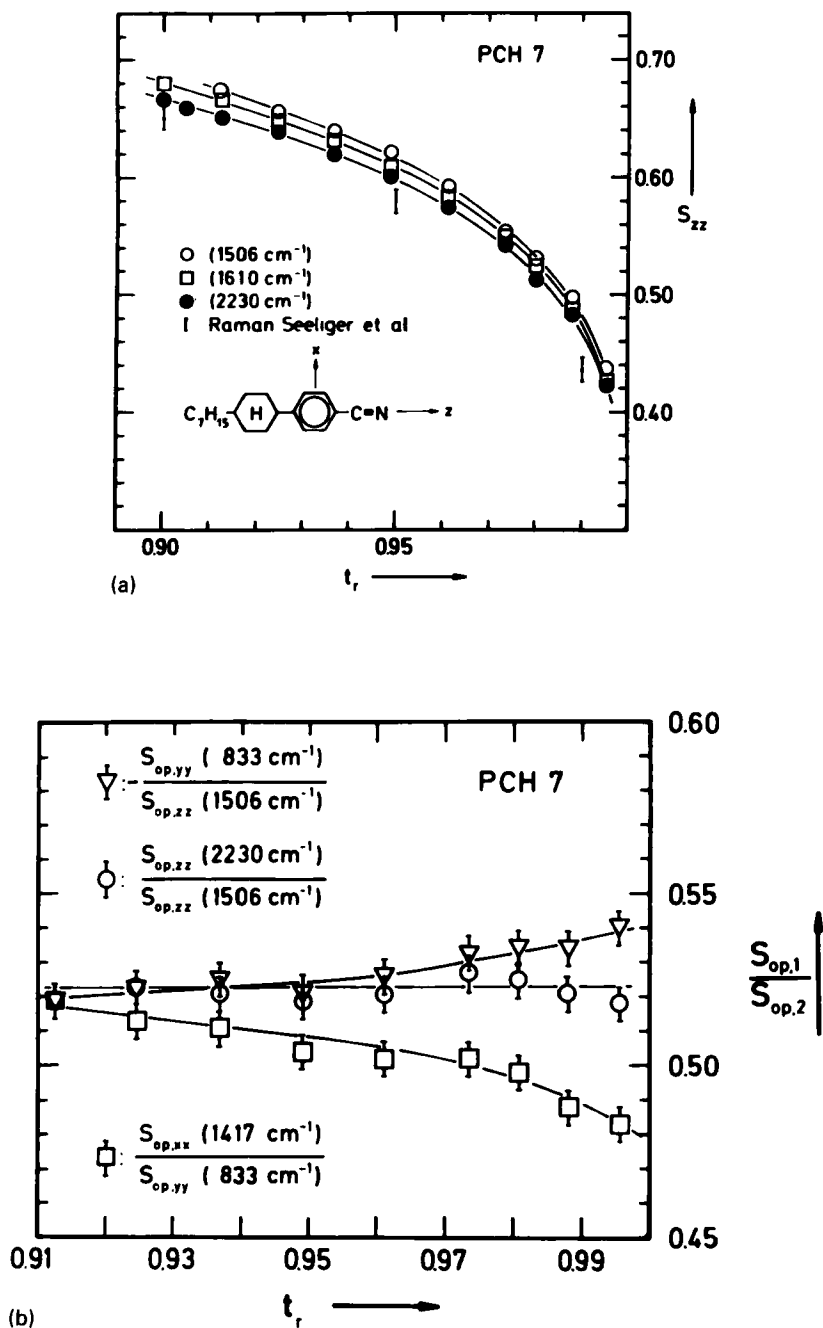


FIGURE 5(a) Order parameter S_{zz} of PCH7 as a function of t_r from the Raman study³⁰ of Seliger (1608 cm^{-1}) and from our IR-dichroism investigations at 1506 cm^{-1} , 1610 cm^{-1} , 2230 cm^{-1} ; (b) $-S_{op,yy}(833 \text{ cm}^{-1})/(S_{op,zz}(1506 \text{ cm}^{-1}))$, $S_{op,zz}(2230 \text{ cm}^{-1})/S_{op,zz}(1506 \text{ cm}^{-1})$ and $S_{op,xx}(1417 \text{ cm}^{-1})/S_{op,yy}(833 \text{ cm}^{-1})$ of PCH7 as a function of reduced temperature. All ratios were normalized to the value of $-S_{op,yy}(833 \text{ cm}^{-1})/(S_{op,zz}(1506 \text{ cm}^{-1}))$ at $t_r = 0.9125$.

the order parameters S_{zz} and $\langle P_4 \rangle$ of PCH7 have been determined.³⁰ Because of the small optical anisotropy, $\Delta n = n_{\parallel} - n_{\perp}$, the influence of the local field correction on the optically determined order parameters should be strongly reduced. Unfortunately, NMR-measurements of PCH7 are not available for comparison with our IR-dichroism data. On the other hand, with PCH7 we have the unique possibility to analyse the second component of the "1500 cm⁻¹-benzene ring-skeleton vibration (1417 cm⁻¹, see Figure 3) whose transition moment is directed parallel to the x -axis. Therefore we can evaluate S_{xx} , S_{yy} , S_{zz} independently and can check the consistency with the mathematical requirement $S_{xx} + S_{yy} + S_{zz} = 0$. Figure 5a shows the order parameter S_{zz} of PCH7 as determined using the Raman method³⁰ and the IR-dichroism method as a function of the reduced temperature. We observe slightly different S_{zz} -values for the various absorption bands in the same sequence as with CB5—namely $S_{zz}(1506 \text{ cm}^{-1}) > S_{zz}(1610 \text{ cm}^{-1}) > S_{zz}(2230 \text{ cm}^{-1})$. We recognize a satisfactory agreement of our data with the values from the Raman measurement of Seeliger,³⁰ although his order parameters are slightly lower. The order parameters S_{zz} , S_{yy} , S_{xx} and D , as determined by the dichroism of the absorption bands at 1506 cm⁻¹, 833 cm⁻¹ and 1417 cm⁻¹ respectively, are listed in Table Ia. Only two of the three order parameters are independent. Choosing S_{zz} and S_{yy} as independent variables and using the condition $S_{xx} + S_{yy} + S_{zz} = 0$, we calculated $S_{xx}(\text{cal})$ and $D(\text{cal}) = S_{xx}(\text{cal}) - S_{yy}(833 \text{ cm}^{-1})$. Both quantities are also given in Table Ia. There exists a remarkably good correspondence between $D(\text{meas})$ and $D(\text{cal})$. The comparison with CB5 reveals that D of PCH7 is smaller by a factor 2. This seems very reasonable, because PCH7 with its cyclohexane ring and its longer alkyl chain should show more rotational symmetry than CB5. The various ratios of the optical order parameters as a function of the reduced temperature are depicted in Figure 5b. $S_{\text{op},zz}(2230 \text{ cm}^{-1})/S_{\text{op},zz}(1506 \text{ cm}^{-1})$ is, as expected, independent of temperature. The ratio $S_{\text{op},xx}(1417 \text{ cm}^{-1})/S_{\text{op},yy}(833 \text{ cm}^{-1})$ shows a distinct temperature dependence of about 10%. As the bands at 1417 cm⁻¹ and 833 cm⁻¹ possess the same sign and nearly the same magnitude of dichroism according to Equation (4), the local field correction can change this ratio only insignificantly. In our opinion this confirms that $D \neq 0$ holds. From the temperature dependence of the ratio $-S_{\text{op},yy}(833 \text{ cm}^{-1})/S_{\text{op},zz}(1506 \text{ cm}^{-1})$ one could also conclude that D must be different from zero, but according to Equation (3), this ratio is more sensitive for a local field correction.

It is very instructive to see how any local field correction with $g > 1$ changes the results for PCH7. We have again applied the Vuks correction. Table Ib contains the analogous corrected order parameters as given in Table Ia. In addition, the Vuks correction factor g_v is listed. Taking this correction into account we observe a distinct discrepancy between $S_{xx}^v(1417 \text{ cm}^{-1})$ and $S_{xx}^v(\text{cal})$ and consequently between $D^v(\text{meas})$ and $D^v(\text{cal})$. As expected there is no essential difference between $D(\text{meas})$ and $D^v(\text{meas})$, as the correction has only a negligible influence on the D -values if absorption bands with the same sign of dichroism and nearly the same magnitude of dichroism are used. On the other hand $D^v(\text{cal})$ approaches zero when the Vuks correction is applied. By summing up the figures $S_{xx}(1417 \text{ cm}^{-1})$, $S_{yy}(833 \text{ cm}^{-1})$ and $S_{zz}(1506 \text{ cm}^{-1})$, we ascertain that our uncorrected infrared-dichroism data are consistent with the mathematical requirement $S_{xx} + S_{yy} + S_{zz} =$

TABLE Ia

Order parameters S_{xx} , S_{yy} , S_{zz} , $D(\text{meas}) = S_{xx} - S_{yy}$, $S_{xx}(\text{cal})$ and $D(\text{cal})$ for PCH7. In addition $S_{xx} + S_{yy} + S_{zz}$ is given. $S_{xx}(\text{cal})$ and $D(\text{cal})$ have been calculated from the relations $S_{xx}(\text{cal}) + S_{yy}(833 \text{ cm}^{-1}) + S_{zz}(1506 \text{ cm}^{-1}) = 0$ and $D(\text{cal}) = S_{xx}(\text{cal}) - S_{yy}(833 \text{ cm}^{-1})$.

t_{red}	$S_{zz}(1506 \text{ cm}^{-1})$	$S_{yy}(833 \text{ cm}^{-1})$	$S_{xx}(1417 \text{ cm}^{-1})$	$S_{xx} + S_{yy} + S_{zz}$	$D(\text{meas})$	$S_{xx}(\text{cal})$	$D(\text{cal})$
0.9125	0.674	- 0.350	- 0.319	0.005	0.031	- 0.324	0.026
0.9245	0.657	- 0.343	- 0.309	0.005	0.034	- 0.314	0.029
0.9367	0.640	- 0.336	- 0.301	0.003	0.035	- 0.304	0.032
0.949	0.622	- 0.324	- 0.287	0.011	0.037	- 0.298	0.026
0.9612	0.593	- 0.312	- 0.275	0.006	0.037	- 0.281	0.031
0.9375	0.554	- 0.296	- 0.261	- 0.003	0.035	- 0.258	0.038
0.9808	0.531	- 0.283	- 0.248	0.000	0.035	- 0.248	0.035
0.9881	0.498	- 0.266	- 0.228	0.004	0.038	- 0.232	0.034
0.9955	0.439	- 0.237	- 0.201	0.001	0.036	- 0.202	0.035

TABLE Ib

The order parameters from Table Ia were corrected by the Vuks field correction factor $g_v = n_v/n_i$ (see equation 5 and ref. 20). We used refractive indices measured at $\lambda = 0.633 \mu\text{m}$. In addition, $S_{xx}^V + S_{yy}^V + S_{zz}^V$ is given in the Table.

t_{red}	$g_v = \frac{n_v}{n_i}$	$S_{zz}^V (1506 \text{ cm}^{-1})$	$S_{yy}^V (833 \text{ cm}^{-1})$	$S_{xx}^V (1417 \text{ cm}^{-1})$	$S_{xx}^V + S_{yy}^V + S_{zz}^V$	$D^V(\text{meas})$	$S_{xx}^V (\text{cal})$	$D^V(\text{cal})$
0.9125	1.077	0.692	- 0.340	- 0.309	0.043	0.031	- 0.352	- 0.012
0.9245	1.072	0.675	- 0.332	- 0.297	0.046	0.035	- 0.343	- 0.011
0.9367	1.070	0.657	- 0.326	- 0.289	0.042	0.037	- 0.331	- 0.005
0.949	1.068	0.640	- 0.314	- 0.274	0.052	0.038	- 0.326	- 0.012
0.9612	1.065	0.613	- 0.301	- 0.262	0.050	0.039	- 0.312	- 0.011
0.9375	1.061	0.573	- 0.285	- 0.249	0.039	0.036	- 0.288	- 0.003
0.9808	1.059	0.549	- 0.272	- 0.235	0.042	0.037	- 0.277	- 0.005
0.9881	1.056	0.515	- 0.256	- 0.215	0.044	0.041	- 0.259	- 0.003
0.9955	1.050	0.456	- 0.226	- 0.188	0.042	0.038	- 0.230	- 0.004

0 (see Table Ia). If any local field correction with $g > 1$ (but also with $g < 1$) is applied, an increasing deviation from the above sum condition is obtained (see $S_{xx}^v + S_{yy}^v + S_{zz}^v$ in Table Ib).

Our experimental results for CB5 (large optical anisotropy) and PCH7 (small optical anisotropy) are compatible with a small local field correction $1 < g < g_v$ whose amount is comparable with our measuring accuracy and therefore may be neglected.

Based on these results, the order parameters S_{zz} and D of the various liquid crystal classes shown in Figure 2 were calculated disregarding local field effects.

2. Influence of the ring system on the order parameters S_{zz} and D

The order parameters S_{zz} and D for the binary terminally polar mixtures CB7/5, PCH 7/5, CCH7/5, CPP7/5 and PDX7/5 are shown in Figures 6–8. The S_{zz} -values for CB7/5 and PCH7/5 as determined with the various absorption bands exhibit the same small but systematic difference already observed with CB5 and PCH7.

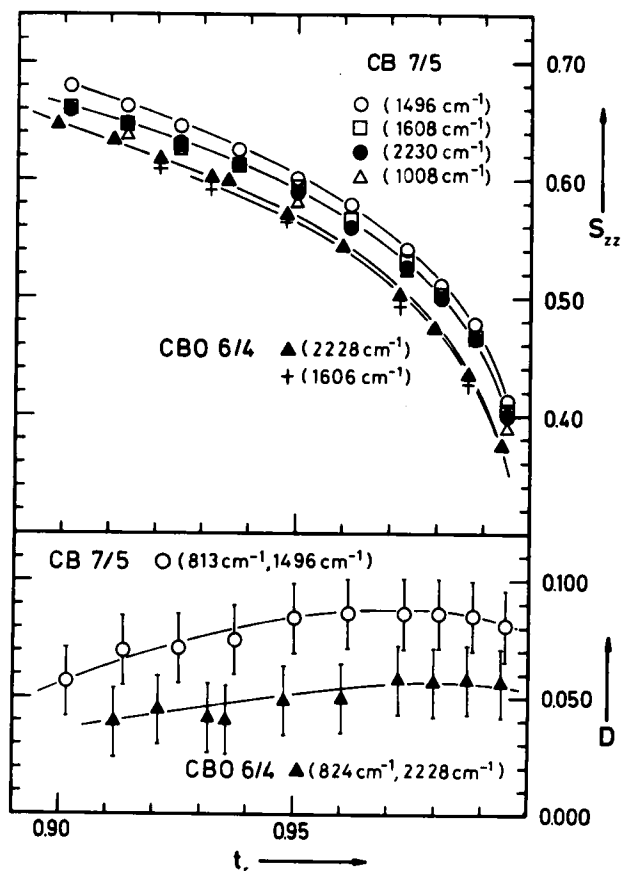


FIGURE 6 Order parameters S_{zz} and D for CB7/5 and CB06/4 as a function of t_r .

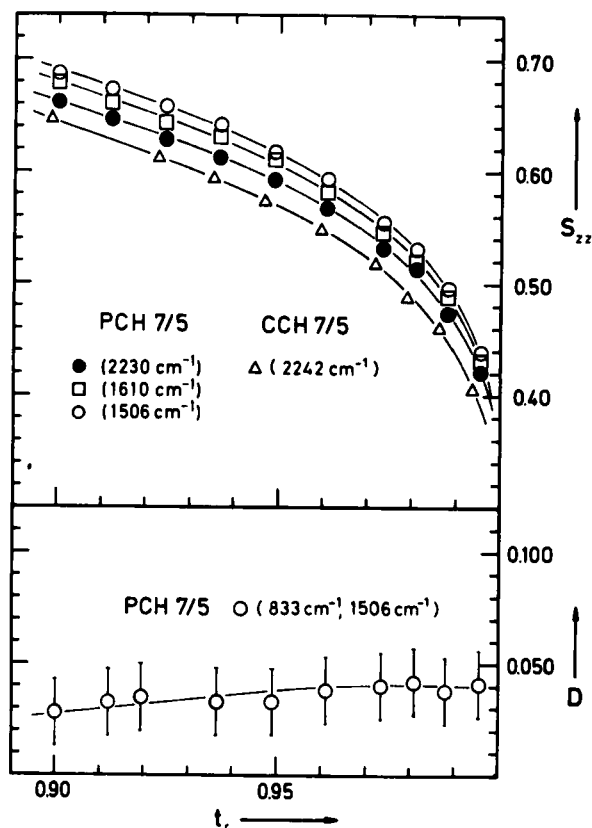


FIGURE 7 Order parameters S_{zz} and D for PCH7/5 and S_{zz} of CCH7/5 as a function of t_r .

The S_{zz} -values for CB7/5 are only a little larger than those for CB5, suggesting that the heptyl component is only slightly more highly ordered than the pentyl component. The same is true for the PCH's as S_{zz} (PCH7) $>$ S_{zz} (PCH7/5) holds. The comparison of Figure 6 and Figure 7 reveals no difference worth mentioning in the orientational ordering of CB7/5 and PCH7/5.

The infrared spectra of CCP7/5 and PDX7/5 showed strongly diminished absorption intensities of the benzene ring bands at 1600 cm^{-1} and 1500 cm^{-1} , not allowing the evaluation of S_{zz} from these data. The order parameters S_{zz} of CPP7/5 and PDX7/5 as measured by the cyano-vibration band are comparably large, but are slightly smaller than that of CB7/5.

A remarkable result can be obtained for CPP7/5. The frequencies of the non-planar, C-H-out-of-plane deformation modes of the benzene ring are correlated with the number of hydrogen atoms.²³ This correlation also holds for the corresponding vibrational modes of the pyrimidine ring. The *para*-disubstituted benzene ring contains two isolated pairs of hydrogen atoms, whereas the pyrimidine system possesses only two isolated H-atoms. In the IR-spectrum of CPP7/5, one would expect two different C-H absorption bands where the high frequency vibrational

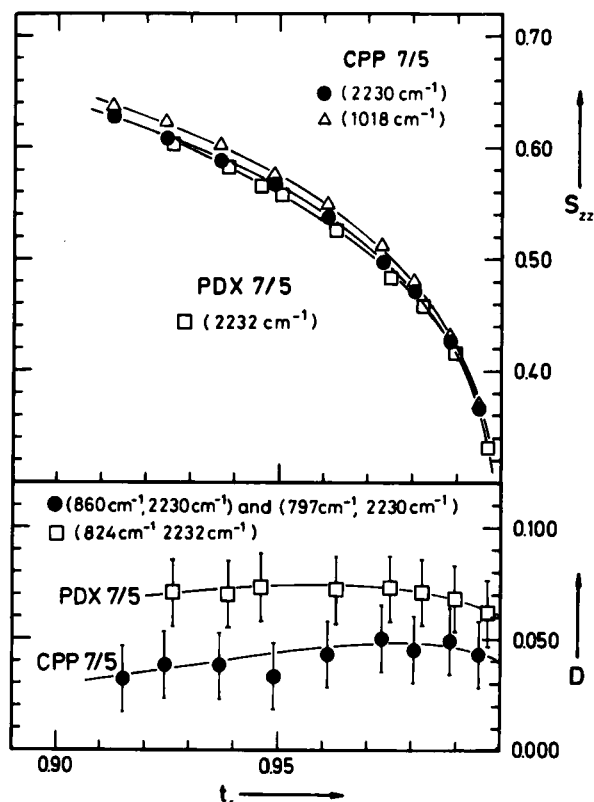


FIGURE 8 Order parameters S_{zz} and D for CPP7/5 and PDX 7/5 as a function of t_r . The vibrational modes at 860 cm^{-1} and 797 cm^{-1} were assigned to the benzene and the pyrimidine ring of CPP7/5. The absorption band at 824 cm^{-1} belongs to the benzene ring of PDX7/5.

mode should belong to the benzene ring. In fact we could observe two bands with negative dichroism at 860 cm^{-1} and 797 cm^{-1} . If our assignment is correct, $D(860\text{ cm}^{-1})$ and $D(797\text{ cm}^{-1})$ represent the molecular biaxialities of the benzene ring and the pyrimidine ring respectively. As Figure 8 shows, we obtain $D_{\text{Pyrimidine}} \approx D_{\text{benzene}} > 0$. Because D is non-zero, we can conclude that within our measuring accuracy both ring systems must be coplanar.

The order parameter D for PDX7/5 was determined from the C-H-out-of-plane deformation mode of the benzene ring. Analogous C-H-out-of-plane deformation modes of the dioxan ring were observed, but showed only weak absorption strength.

Figure 7 contains additionally the order parameter S_{zz} of CCH7/5 as determined from the cyano-vibration band. S_{zz} (CCH7/5) is insignificantly lower than that of PCH7/5.

In the absorption spectrum of CCH7/5 we observed at 898 cm^{-1} a band with negative dichroism. This band has been assigned to CH_2 rocking vibrations of the cyclohexane ring systems,³¹ and was also recorded in the infrared spectrum of

PCH7/5. As the direction of the transition moment of this vibration is not exactly known, we will not publish values of the order parameter D for CCH7/5.

Summarizing the influence of the ring systems on S_{zz} , we ascertain comparable orientational ordering of CB7/5 and PCH7/5. Substituting a pyrimidine or a dioxan ring for a benzene ring (CPP7/5 or PDX7/5) diminishes S_{zz} only slightly. Moreover, the S_{zz} values of CPP7/5 and PDX7/5 agree very well. If we replace both benzene rings by cyclohexane rings (CCH7/5), we observe only a small decrease of S_{zz} .

All components represented in Figures 6–8 exhibit molecular biaxiality because $D \neq 0$ holds. D has only a weak temperature dependence and all curves have a similar form. PCH7/5 and CPP7/5 show only weak deviation from rotational symmetry, whereas CB7/5 and PDX7/5 reveal larger biaxiality.

3. Influence of an alkoxy chain or an ester group on S_{zz} and D

The results for CB06/4 which contains an alkoxy chain instead of an alkyl chain are depicted additionally in Figure 6. The S_{zz} -values derived from the cyano- and the benzene-ring bands agree very well and are smaller than that of CB7/5. The molecular biaxiality of CB06/4 seems to be less pronounced than that of CB7/5. Figure 9a illustrates directly the alteration ΔS_{zz} when the alkyl chain is replaced by an even-numbered (CB06/4) or an odd-numbered alkoxy chain (CB07/5). As can distinctly be seen, the orientational order of the alkoxy substituted compound CB06/4 and the longer chain representative CB07/5 is considerably lower than S_{zz} of the alkyl substituted mixture CB7/5.

Inserting an additional ester group between the benzene-rings of CB7/5 leads to the cyano-ester CPE7/5 as shown in Figure 10. The S_{zz} -values derived from the dichroism of the cyano-absorption (2234 cm^{-1}) are larger than those evaluated from the benzene ring bands at 1506 cm^{-1} and 1604 cm^{-1} . The interaction of the ester group with the two aromatic rings leads to a weak doublet splitting of the benzene ring bands. But the splitting cannot be spectrally resolved. Therefore the analysis is more difficult to make, and the S_{zz} -values determined are more faulty. In spite of this uncertainty, we cannot exclude that the directions of the transition moments of the “ 1600 cm^{-1} ” and the “ 1500 cm^{-1} ” benzene ring absorptions are changed by the interaction of the benzene ring with the ester group and are no longer parallel to the z -axis, but instead make a small angle to the z -axis. In future, we will therefore always use the S_{zz} -values derived from the cyano-absorption. The ester group influences also the absorption spectrum originating from the non-planar C-H-deformation modes. We observe two absorption bands at 882 cm^{-1} and 785 cm^{-1} with considerable substructure. Therefore the background line cannot be drawn with the usual precision. Furthermore, we cannot assign the two different bands to both the aromatics respectively, and the angle between the two benzene ring planes is not well known. For that reason the latter is not taken into account in our evaluation. With all these difficulties, the computed values of the order parameter D possess larger limits of error than the D -values of the compounds without an ester group. Nevertheless with the 882 cm^{-1} and the 785 cm^{-1} absorption band we determine about the same order parameter D . Figure 10 shows that CPE 7/5 behaves as nearly cylindrically symmetric, because D is only slightly

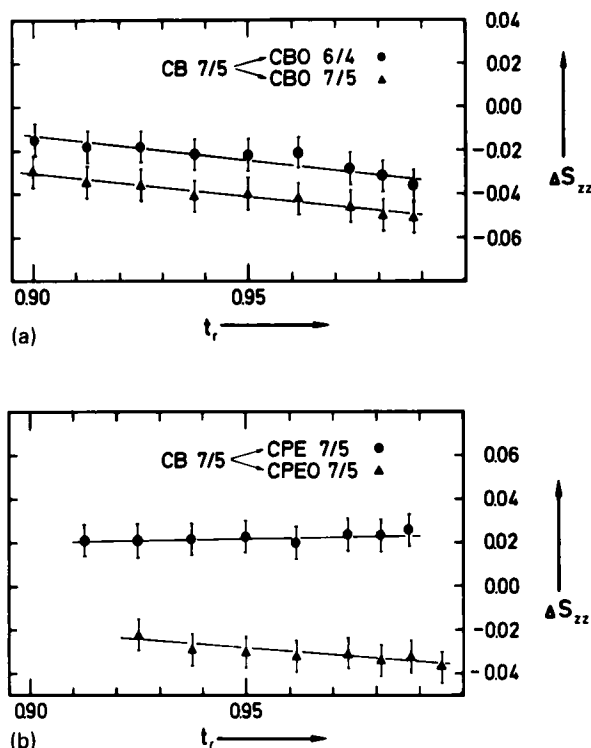


FIGURE 9(a) Change ΔS_{zz} of S_{zz} as a function of t_r for the replacement of the alkyl chain of CB7/5 by an alkoxy chain (CB06/4, CB07/5); (b) Change ΔS_{zz} of S_{zz} as a function of t_r for the insertion of an additional ester group between the two benzene rings of CB7/5 leading to the ester CPE7/5. Furthermore the change of S_{zz} by the replacement of the alkyl chain of CPE7/5 by an alkoxy chain (CPE07/5) is illustrated in the figure.

different from zero. Everything that has been said about the influence of the ester group on the benzene ring vibrations applies also to CPE07/5, which contains additionally an oxygen atom between the benzene ring and the terminal alkyl chain. The results are very similar to CPE7/5 and are also depicted in Figure 10. Again the S_{zz} -values determined from the bands at 1605 cm^{-1} and 1513 cm^{-1} are lower than the values from the cyano-absorption at 2232 cm^{-1} . The comparison of CPE7/5 with CB7/5 and with CPE07/5 is illustrated by the change ΔS_{zz} in Figure 9b. CPE7/5 possesses a larger average molecular length and a higher degree of orientational order than CB7/5. A remarkable decrease of the orientational order results if the alkyl chain of CPE7/5 is replaced by an alkoxy chain producing the nematogen CPE07.5.

4. Influence of the terminally polar cyano group on S_{zz} and D

Figure 11 contains S_{zz} and D values for the terminally non-polar mixture DXP 504/502 as a function of the reduced temperature. With DXP 504/502, we observe strong benzene ring absorptions at 1616 cm^{-1} and 1517 cm^{-1} in contrast to the

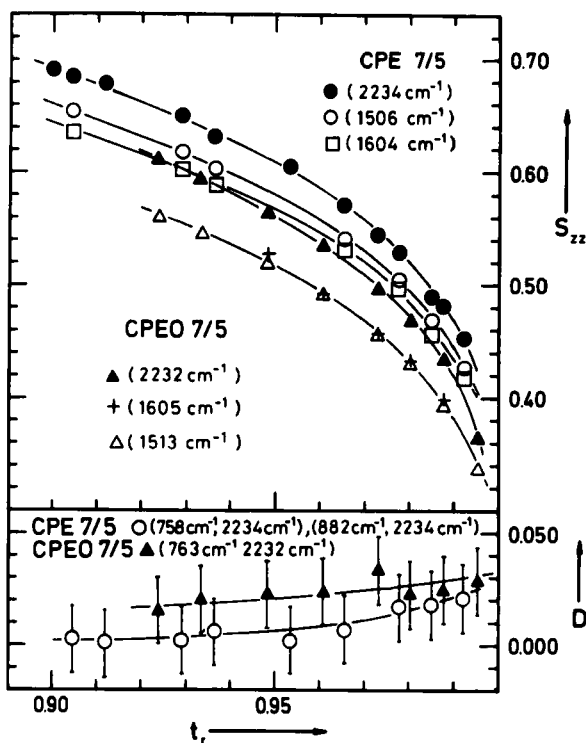


FIGURE 10 Order parameters S_{zz} and D of CPE7/5 and CPEO7/5 as a function of t_r .

terminally polar mixture PDX7/5. Moreover we analysed the dichroism of a strong absorption band at 1387 cm^{-1} . One recognizes a very satisfactory agreement among the S_{zz} -values evaluated from the dichroism of the various bands (1616 cm^{-1} , 1517 cm^{-1} , 1387 cm^{-1}). The absorption band at 1387 cm^{-1} was also observed in the spectrum of PDX7/5, but could not be evaluated because it overlapped with other bands. Because of the good correspondence with the dichroism of the benzene ring bands, we think that this band must be assigned to a dioxan ring skeletal vibration with its transition moment direction nearly parallel to the z -axis. For comparison S_{zz} and D of the analogous terminally polar mixture PDX7/5 are presented additionally in Figure 11. Apparently the substitution of the strongly polar cyano-group by a longer alkoxy chain leads to a distinct enhancement of the orientational order parameter S_{zz} , whereas D slightly decreases.

S_{zz} and D values for the terminally non-polar nematic PYP606 are depicted in Figure 12. There exists an excellent agreement between the S_{zz} -values evaluated from the benzene ring band at 1516 cm^{-1} , the carbon-oxygen stretching vibration band at 1252 cm^{-1} and an absorption band at 1329 cm^{-1} . This latter band has probably to be assigned to a pyrimidine ring skeletal vibration, because only with CPP7/5 could we also observe an absorption at this wavelength, but with strong reduced intensity. Furthermore, the transition moment should point nearly parallel

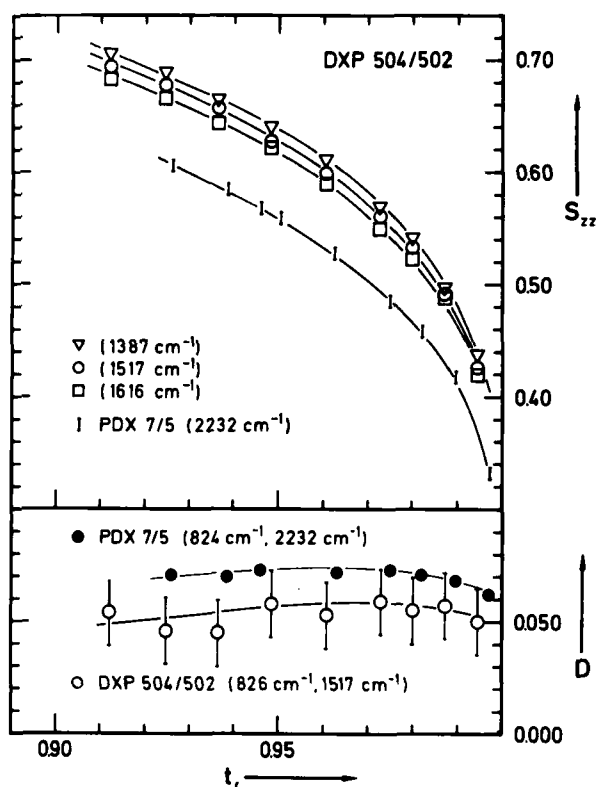


FIGURE 11 Order parameters S_{zz} and D of DXP504/502 as a function of t_r . For comparison, the results for the corresponding terminally-polar mixture PDX7/5 are depicted in the figure.

to the *para*-axis of the benzene ring because the order parameters calculated from the bands at 1516 cm^{-1} and 1329 cm^{-1} agree very well. The comparison with the terminally polar compound CPP 7/5 demonstrates once again the strong influence of the polar cyano-group on the orientational ordering. S_{zz} increases by more than 0.10 when the cyano-group is replaced by a long alkoxy chain. Moreover the order parameter D seems to be slightly smaller for PYP 606 than for CPP 7/5. Explaining the high orientational order of the terminally non-polar compounds DXP504/502 and PYP606, we suppose that strong laterally attractive interactions between the long alkyl chains are effective. It is interesting to note that both these substances possess a small ratio of the elastic constants of bend and splay, K_{33}/K_{11} . The latter result has been explained by strong short-range, smectic-like, pair-wise correlations in the nematic phase.³³ As a consequence of the smectic-like pair-wise correlations, one could propose an increase in the short range orientational ordering, and this could possibly cause an enhancement of the long range orientational order. Going to homologues of pyrimidines with longer alkyl chains, the short range smectic-like pair-wise correlations become finally strong enough so that smectic long range order is established.

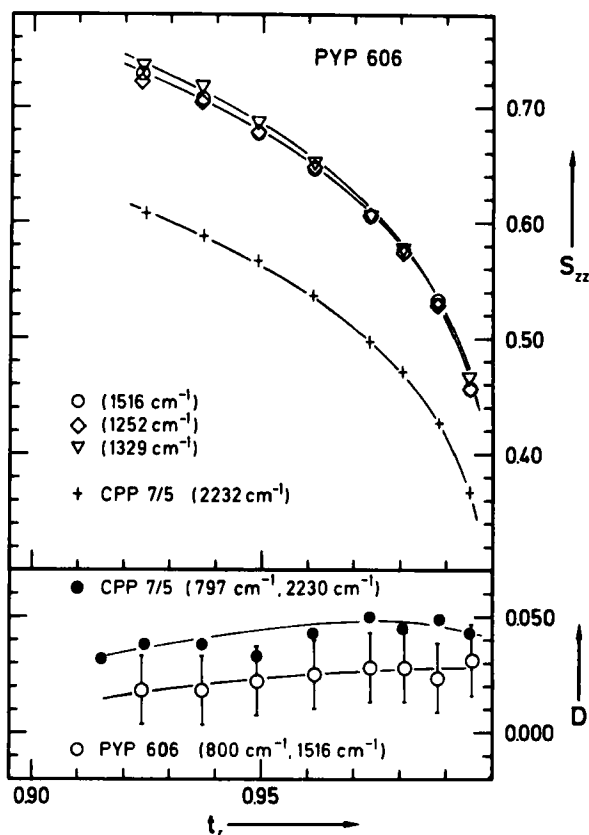


FIGURE 12 Order parameters S_{zz} and D of PYP606 as a function of t_r . For comparison, the results for the corresponding terminally-polar mixture CPP7/5 are depicted in the figure.

5. Comparison with the molecular field theory of Luckhurst *et al.*

In the molecular field theory of Luckhurst *et al.*,⁷ the deviation from molecular cylindrical symmetry has been taken into account by an additional term in the mean field potential. This theory predicts a relationship between $S_{zz} = \langle P_2 \rangle$ and D which is determined entirely by a parameter λ as given in Figure 13 for $\lambda = 0.1, 0.2$ and 0.3 . For $\lambda = 0$ one obtains the familiar Maier-Saupe potential. According to whether repulsive steric interactions or dispersion forces are made responsible for the molecular biaxiality, the biaxiality parameter λ is related to the length, breadth and width of the molecules or to the components of the molecular polarizability tensor.⁷ Without going further into details, we will compare our experimental results with the theoretical predictions. Figure 13a contains the values of D as a function of $S_{zz} = \langle P_2 \rangle$ for CB5 measured by NMR and IR-dichroism. The IR-data are in closer correspondence to the theoretical curve than the NMR-data. The data of PCH7 fit nicely with the theory with $\lambda = 0.1$. D versus S_{zz} for the various terminally polar and terminally non-polar liquid crystal materials is depicted correspondingly in Figure 13b and Figure 13c. With the exception of CPE7/

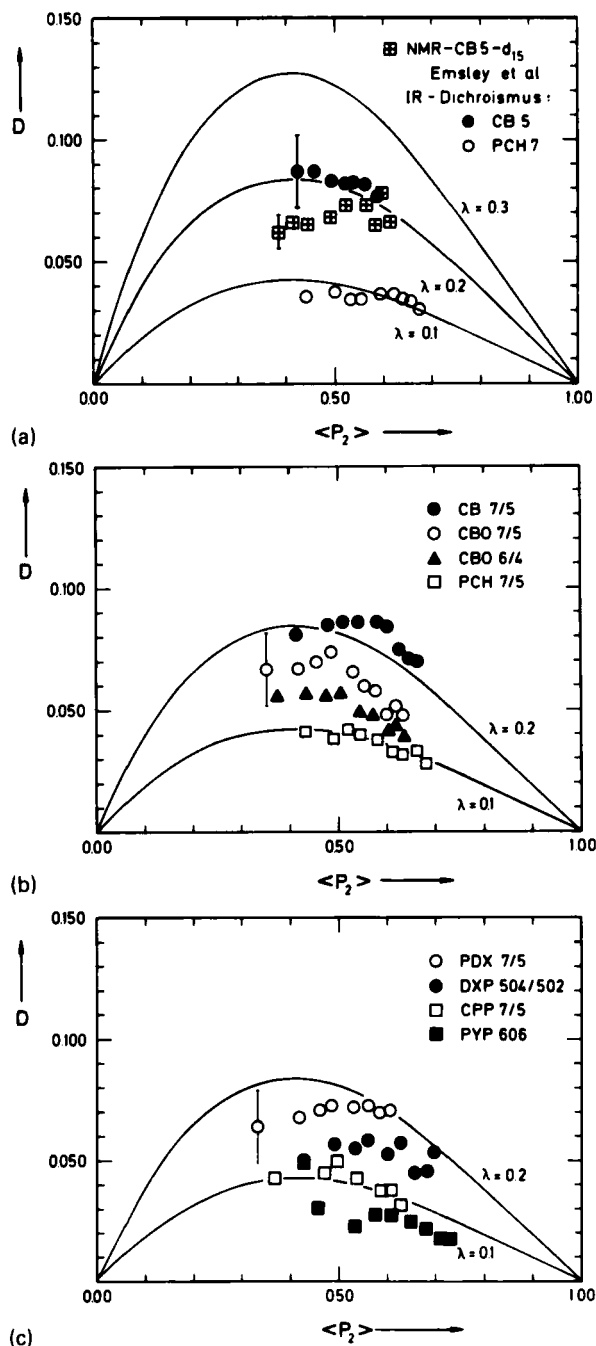


FIGURE 13 Order parameter D as a function of S_{zz} as predicted by the molecular field theory of Luckhurst and Zannoni⁷ for λ -values of 0.1, 0.2 and 0.3 indicated by a continuous line; (a) NMR-study on CB5-d₁₅ by Emsley⁷ (□), infrared dichroism investigations on CB5 (●) and PCH7 (○); (b) Infrared dichroism studies on CB7/5 (●), CB07/5 (○), CB06/4 (▲) and PCH 7/5 (□); (c) Infrared dichroism studies on PDX7/5 (○), DXP504/502 (●), CPP7/5 (□) and PYP 606 (■).

5 and CPE07/5 which seem to behave as nearly rotationally symmetric and are therefore not given in the figures, all the other compounds show a more or less distinctly pronounced molecular biaxiality. Moreover the variation of D with S_{zz} is approximately of the form predicted by the MF-theory of Luckhurst *et al.* with λ -values between 0.1 and 0.2. Estimations of λ from the molecular dimensions of our liquid crystal materials show that this is the correct order of magnitude.

CONCLUSIONS

The infrared dichroism method is a valuable and simple technique for obtaining information about the orientational order parameters S_{zz} and $D = S_{xx} - S_{yy}$ of nematic liquid crystals. The influence of the local field correction, which is the main drawback of the method, was studied first by comparing the IR-data for CB5 with data from NMR-studies, and second by measuring independently for the first time S_{xx} , S_{yy} and S_{zz} for PCH7. From both investigations we must suppose that the necessary local field correction is almost within our measuring accuracy and therefore can be neglected. With this assumption, the order parameters S_{zz} and D for various liquid crystal classes have been calculated. The results can be summarized as follows:

— In general the order parameter S_{zz} as determined by different group vibrations agree very well.

— The influence of the ring system on the order parameters S_{zz} is of minor importance.

— Inserting an oxygen between the alkyl chain and the benzene ring always decreases S_{zz} .

— Putting in an ester group between the two benzene rings slightly increases S_{zz} .

— The replacement of the strongly polar cyano-group by a longer alkoxy group leads to a strong enhancement of the order parameter S_{zz} . We suppose that strong laterally attractive interactions between the long alkyl chains favour the formation of a high orientational order.

— With the exception of CPE7/5 and CPE07/5 all compounds investigated show molecular biaxiality because $D \neq 0$ is observed. In consideration of the large error in the order parameter D , it is however difficult to interpret the influence of molecular structure on D . According to our results, the molecular biaxiality is significantly larger for CB7/5 and PDX7/5 than for CB06/4, CCP7/5, PCH7/5 and CPE7/5 and also slightly larger for the terminally polar compounds PDX7/5 and CPP7/5 than for the terminally non-polar liquid crystals DXP504/502 and PYP 606. Although it seems quite reasonable that the replacement of the stiff cyano-group by a long flexible alkoxy group or the substitution of the flexible cyclohexane ring for the plane benzene ring reduces the molecular biaxiality we must warn against drawing too many conclusions from the data. For example, one has no explanation as to why PDX7/5 with its non-planar dioxan ring behaves more biaxially than CPP7/5 whose two plane ring systems should be nearly coplanar according to our studies.

—The order parameter D shows only a weak temperature dependence and all curves have an approximately similar form as predicted by the molecular field theory of Luckhurst *et al.* with λ -values between 0.1 and 0.2. These λ -values are of the correct order of magnitude for the investigated molecules.

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APPENDIX

We consider molecules containing two non-planar benzene rings. The absorption bands of the benzene ring skeletal vibrations (1600 cm^{-1} , 1500 cm^{-1}) as well as of the C-H-out-of-plane deformation modes for the two benzene rings are not resolved spectroscopically and one observes respectively the superposition of the absorptions of both benzene rings. The angle between the two benzene rings planes is designated as 2γ . We choose the y -direction perpendicular to the angle-bisecting plane of the two aromatic rings, leaving the x - and z -direction unchanged. The directions of the two transition moments \mathbf{M}_1 and \mathbf{M}_2 belonging to the out-of-plane modes differ only in the angle β and are given by:

$$\begin{aligned}\mathbf{M}_1 (\alpha_1 = 90^\circ, \beta_1 = 90^\circ + \gamma) \\ \mathbf{M}_2 (\alpha_2 = 90^\circ, \beta_2 = 90^\circ - \gamma)\end{aligned}\quad (6)$$

Assuming equal absorption probabilities for the two benzene rings and adding separately their respective absorptions for light polarization parallel ($A_{\parallel} = A_{\parallel,1} + A_{\parallel,2}$) and perpendicular to the director \mathbf{n} ($A_{\perp} = A_{\perp,1} + A_{\perp,2}$) the following expression for the average molecular biaxiality \bar{D} can be derived¹⁶.

$$\bar{D} = \frac{\frac{2(1 - \bar{R})}{2 + \bar{R}} - \bar{S}_{zz}}{\cos 2\gamma} \quad \text{with } R = \frac{A_{\parallel,1} + A_{\parallel,2}}{A_{\perp,1} + A_{\perp,2}} \quad (7)$$

and where \bar{D} is averaged over the biaxialities D_1 and D_2 of the two benzene rings:

$$\bar{D} = \frac{D_1 + D_2}{2} \quad (8)$$

The average order parameter \bar{S}_{zz} in Equation (7) is evaluated from an analogous dichroic ratio \bar{R} by averaging either over the two skeletal vibrations of the two benzene rings or using the cyano-stretching vibration. In any case, we assume that the corresponding transition moments are parallel and point in the z -direction. If a benzene ring skeletal vibration is taken for the evaluation, \bar{S}_{zz} is given by:

$$\bar{S}_{zz} = \frac{S_{zz,1} + S_{zz,2}}{2} \quad (9)$$

where $S_{zz,1}$ and $S_{zz,2}$ are the order parameters for the two benzene rings.

For $\gamma = 0$ and $\alpha = \beta = 90^\circ$, Equations (2) and (7) become equivalent. If the two benzene ring planes stand perpendicular to one another ($2\gamma = 90^\circ$), the molecular biaxiality parameter \bar{D} should become zero for symmetry reasons. In that case, Equation (7) cannot be used, because the denominator disappears for $2\gamma = 90^\circ$. Applying Equation (7) to CB5, CB7/5, CB06/4 and CB07/5, we assume $2\gamma = 32^\circ$.²⁷ Formula (7) then shifts our measured order parameter D by 17% to higher values.