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Optical Studies of the Anisotropic Solute-Solvent Interaction in Liquid Crystals†

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Abstract—"Compensated" nematic mixtures of cholesteryl derivatives are well suited as anisotropic solvents for optical experiments in the ultraviolet. The average orientations of a great number of aromatic molecules in a nematic mixture of cholesteryl chloride and cholesteryl laurate at 30 °C have been determined by absorption polarization studies.

Our attempts to correlate the elements of the Saupe order matrix of these molecules with their physical properties yielded the following results:

1) For some elongated molecules a linear relation holds between the average orientation of the long molecular axis and the molecular dimensions, while large deviations from this correlation are observed for molecules with easily polarizable substituents.

2) The order parameters are directly related to the principal solute polarizabilities of the solute molecules which can be determined with good accuracy from the order matrix elements.

We conclude from these results that repulsive forces do not contribute considerably to the anisotropic solute–solvent interaction potential. It is further shown that relative order parameters in cholesteric solvents can be determined by measurement of the circular dichroism caused by the solute absorption.

1. Introduction

An important field of application of liquid crystals is their possible use as anisotropic solvents to prepare systems of homogeneously oriented solute molecules for spectroscopic studies of the anisotropy of physical molecular properties. A well known example of this type of application of liquid crystals is the determination of the geometry of molecules from their high resolution NMR spectra in nematic

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liquid crystals (cf. Ref. 1). In our laboratory liquid crystals have been used extensively to determine the orientation of the transition moments of optical transitions in aromatic molecules and molecular complexes.(2,4,6) Such measurements are of great importance since the knowledge of the polarization directions of optical transitions is essential for an understanding of the nature of excited molecular states. In addition, absorption spectra taken in anisotropic solvents yield in a very simple way information on weak hidden absorption bands.

It is the primary goal of the present paper to show that these polarization experiments yield a very simple method of determining the average orientation of a large class of aromatic molecules. The solute molecules can thus be considered as optical probes to study the anisotropy of the solute–solvent interaction. By comparing the average orientation of a large number of different solute molecules it is possible to learn more about the nature of the anisotropic solute–solvent interaction. Two types of polarization experiments can be performed. The first method is based on the measurement of the linear dichroism in electric field oriented "compensated" nematic mixtures of cholesteryl derivatives. The second method is based on the determination of the circular dichroism (CD) in partially compensated cholesteric mixtures.(7)

2. The Anisotropic Solvent

Most aromatic molecules absorb strongly in the ultraviolet wavelength region and the liquid crystalline solvents normally used for NMR experiments are therefore not suited for optical polarization studies. The cholesteryl derivatives are to some extent applicable for optical experiments in the ultraviolet since these molecules, which contain only one ethylenic double bond, are transparent to about 240 nm if they are devoid of unsaturated substituents and if they are purified properly.(6) A further advantage of the cholesteryl derivatives is that they represent rather inert solvents which do not cause severe fluorescence and phosphorescence quenching. The use of cholesteryl derivatives as anisotropic solvents is normally avoided due to their cholesteric nature. However, it is well known that "compensated" nematic mixtures can be prepared in a wide temperature range by mixing cholesteryl chloride with cholesteryl esters in appropriate amounts.(9) The "compensated" nematic mixtures can be aligned by dc electric fields and therefore large samples of homogeneously ordered solutions can be prepared easily; these may also be frozen to form highly ordered glasses.

In Fig. 1 we have plotted the nematic temperature T_{nem} of a number of "compensated" mixtures of cholesteryl chloride with different cholesteryl esters and with *n*-hexyloxy-azoxybenzene (curve 1)† as function of the molar percentage of cholesteryl chloride. According to Fig. 1 the nematic temperature T_{nem} decreases linearly with increasing content of cholesteryl chloride and the whole nematic temperature range can be swept by only small changes in the composition of the mixtures. It is further found that the slopes of the straight lines of Fig. 1 are about the same for all mixtures with cholesteryl esters containing saturated alkyl chains and that the molar percentage of cholesteryl chloride necessary to compensate the twist of the cholesteryl esters at a given temperature increases with increasing length of the CH_2-chains. This is most clearly seen in Fig. 2 where we plotted the molar percentage of cholesteryl chloride as function of the molecular weights of the cholesteryl esters for $T = T_{\text{nem}} = 40\,^{\circ}\text{C}$. According to Fig. 2 the molar percentage of cholesteryl chloride necessary to compensate the twist of the cholesteryl esters increases linearly with the molecular weight of the ester.

The measurements of the linear dichroism reported in this work were all performed with a 1.85 to 1 by weight mixture of cholesteryl chloride and cholesteryl laurate which is nematic at about $T = 30\,^{\circ}\text{C}$. At this temperature the mixture is in an undercooled metastable state, and crystallizes very slowly after several hours.

The homogeneous orientation of the "compensated" mixtures was achieved by applying dc electric fields of the order of 10,000 V/cm. By using such strong electric fields, homogeneously ordered nematic phases can also be prepared from partially compensated large pitch

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† The compensation of the helical twisting of cholesteryl chloride by a non-chiralic compound has also been noted by Saeva *et al.*(8) This result clearly indicates that the sign and the size of the helical twist of cholesteryl chloride strongly depends on the average distance of the chiralic molecules and that the "twisting power" of a molecule is not necessarily an intrinsic molecular property as has been stated by Baessler *et al.*(9)

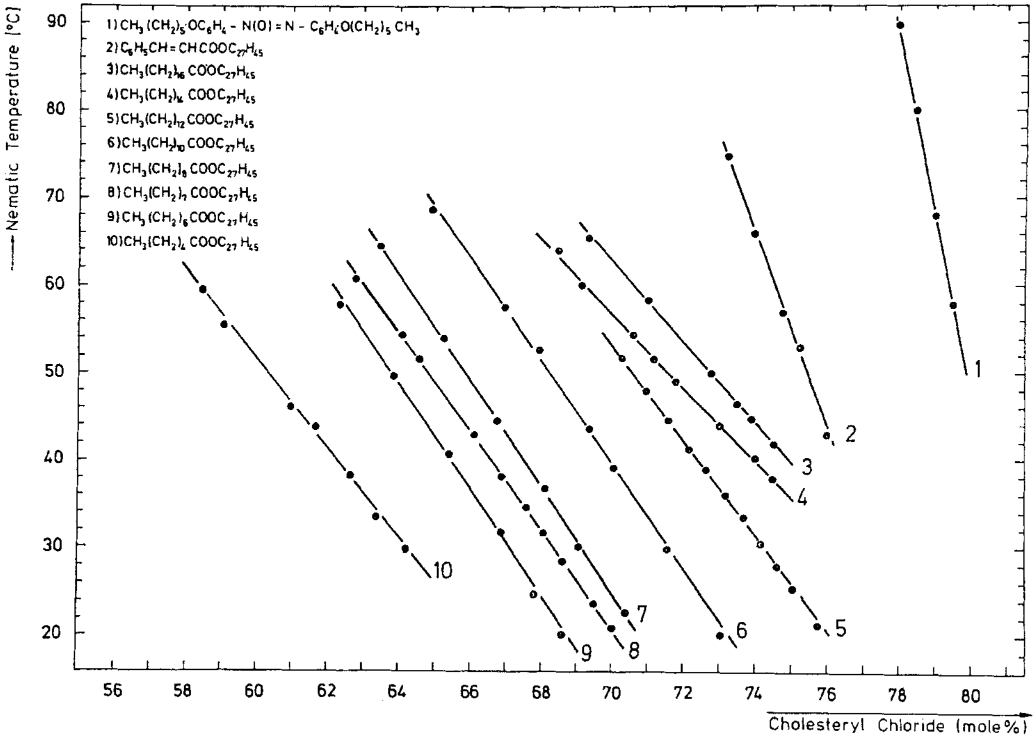

Figure 1. Nematic temperature T_{nem} of several mixtures of cholesteryl chloride (CC) with different cholesteryl esters and with n-hexyloxyazoxybenzene (Curve 1). The nematic temperature is plotted as function of the molar percentage of cholesteryl chloride. T_{nem} has been determined with a polarizing microscope by inspection of the texture.

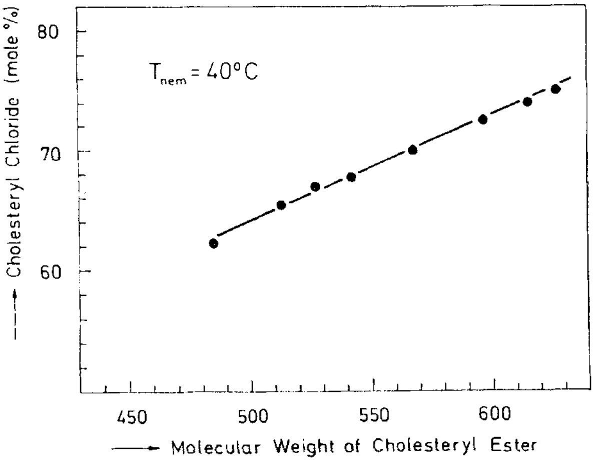

Figure 2. The molar content of cholesteryl chloride in "compensated" nematic mixtures with cholesteryl esters containing alkyl-groups of different chain lengths plotted as function of the molecular weight (chain length) of the ester. The dots are the values taken from Fig. 1 for the nematic temperature $T_{\mathrm{nem}} = 40\,°\mathrm{C}$.

(pitch $> 10\,\mu$m) cholesterics due to the electric field induced cholesteric → nematic transitions. This cholesteric → nematic transition facilitates considerably the application of the "compensated" mixtures as anisotropic solvents since it is difficult to distinguish between nearly compensated (pitch larger than $20\,\mu$m) and truly compensated (nematic) mixtures.

For the measurements of the linear dichroism flat quartz cells with the inner dimensions 0.5×0.4 cm and with an optical path length of about 0.03 cm were used. The side walls of these cuvettes were made of metal (copper or brass) and served as electrodes. The electrode distance was thus 0.5 cm. The absorption polarization spectra were taken in a Cary 14 spectrophotometer using Polacoat 105 UV polarizing filters. The experimental setup will be described in more detail in a forthcoming paper.(6)

3. Determination of the Order Parameters

A. LINEAR DICHROISM

In the following we consider aromatic molecules possessing at least two perpendicular planes of symmetry, i.e. molecules with C_{2v}- or

D_{2h}-symmetry. The optical absorption spectra of aromatic molecules are composed of several electronic absorption bands originating from transitions between the molecular ground state and the excited molecular states, where each electronic band consists of a superposition of vibrational bands corresponding to transitions between the vibrational levels of each electronic state. In the symmetric aromatic molecules considered here, all electronic transitions are polarized parallel to any of the symmetry axes lying in the molecular plane (cf. Ref. 10). However, due to the vibrationally induced mixing of excited electronic states of different symmetry each electronic transition contains vibrational bands of different polarization directions.(10)

In the absorption polarization experiments the optical density (OD) is recorded with the measuring light polarized either parallel ($\mathrm{OD}_{\parallel}$) or perpendicular ($\mathrm{OD}_{\perp}$) to the orienting electric field which is parallel to the optical axis of the ordered liquid crystal. The optical density is expressed in terms of the molar extinction coefficient ϵ, of the concentration c and of the path length d by the equation

$$\mathrm{OD}(\lambda) = \epsilon(\lambda)cd$$

In a forthcoming paper it will be shown that in general the molar extinction coefficients for light polarized parallel ($\epsilon_{\parallel}$) or perpendicular ($\epsilon_{\perp}$) to the electric field are given by

$$\epsilon_{\parallel} = \bar{\epsilon} + \tfrac{2}{3}(\epsilon_x S_{xx} + \epsilon_y S_{yy} + \epsilon_z S_{zz}) \qquad (1a)$$

and

$$\epsilon_{\perp} = \bar{\epsilon} - \tfrac{1}{3}(\epsilon_x S_{xx} + \epsilon_y S_{yy} + \epsilon_z S_{zz}). \qquad (1b)$$

ϵ_x, ϵ_y and ϵ_z are the molar extinction coefficients in the direction of the molecular symmetry axes x, y, and z respectively and $\bar{\epsilon} = \frac{1}{3}(\epsilon_x + \epsilon_y + \epsilon_z)$. S_{xx}, S_{yy} and S_{zz} are the elements of the Saupe order matrix,(11) and are a measure of the average orientation of the x, y and z-axis with respect to the optical axis. According to Eqs. (1a) and (1b) the degree of polarization

$$N = OD_{\parallel}/\mathrm{OD}_{\perp} \qquad (2)$$

depends in general on five independent parameters (ϵ_x, ϵ_y, ϵ_z, S_{zz}, $S_{xx} - S_{yy}$).† One of these parameters can be determined from the

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†In the derivation of this equation the birefringence of the liquid crystal matrix has been neglected (cf. Ref. 6).

absorption spectrum in an isotropic medium where the optical density is given by OD $= \epsilon cd$. In most cases there can be found vibrational bands in the spectrum which are purely polarized parallel to an inplane symmetry axis and which do not overlap appreciably with other vibrational bands. The average orientation of the corresponding symmetry axis can be determined from the value of the degree of polarization N by the equation

$$S_{x_i x_i} = \frac{N-1}{N+2} \tag{3}$$

The so-called O–O-transitions between the vibrational ground levels of the electronic states normally represent such "purely" polarized bands in the spectrum. All three order matrix elements of molecules with C'_{2v}- or D_{2h}-symmetry can be determined if two perpendicularly polarized O–O-bands appear in the spectrum. In favorable cases it is also possible to determine the average orientation of one molecular axis of asymmetric molecules (cf. Ref. 6 and Fig. 4).

B. Circular Dichroism

The appearance of a very strong circular dichroism in the absorption region of non optically active solute molecules dissolved in cholesteric liquid crystals was first reported by Saeva and Wysocky.(8) It has been suggested recently(7) that the origin of this strong circular dichroism is due to the helical arrangement of the solute molecules. A proposed theoretical model (based on the De Vries theory) predicts that the strength of the circular dichroism depends critically on the pitch of the cholesteric phase. The results of this theoretical model may be summarized as follows:

In the Cary 60 spectrometer the CD is recorded in terms of the ellipticity θ (expressed in degrees) which is defined as the arctangent of the ratio of minimum to maximum axis of the elliptically polarized light emerging from the circular dichroic sample. Two limiting cases may be considered depending on the ratio $\lambda^* = \lambda/\lambda_{\mathrm{max}}$ of the measuring wavelength λ to the wavelength of maximum reflectivity λ_{max} of the cholesteric phase (cf. Ref. 7). If λ^* is large compared to the relative birefringence $\alpha = (n_{\parallel} - n_{\perp})/(n_{\parallel} + n_{\perp})$ the ellipticity is to a good approximation given by the following equation:

$$\tan\theta = \frac{0.25\alpha}{\lambda^*}\tan h\left\{\frac{2.303}{2}cd(\epsilon_{\parallel} - \epsilon_{\perp})\right\} \tag{4}$$

This equation shows that $\tan\theta$ increases linearly with the pitch P ($P = n\lambda_{\max}$) of the cholesteric phase. For very large values of the pitch ($\alpha \gg \lambda^*$) the coefficient before the hyperbolic tangent on the right side of Eq. (4) is given by λ^*/α and therefore the ellipticity decreases with increasing value of the pitch.

If the pitch and the relative birefringence α of the cholesteric phase are known the average solute orientation can be determined from the circular dichroism of "purely" polarized vibrational bands as in the case of the linear dichroism. If two perpendicularly polarized O–O-vibrational bands which are purely polarized parallel to two different symmetry axis x_i and x_j appear in the spectrum, the ratio of the corresponding order parameters can be determined without knowledge of the characteristic parameters α and $\lambda_{\max}$ of the solvent, by the following equation:

$$\frac{S_{x_ix_i}}{S_{x_jx_j}} = \frac{\epsilon_{x_j}\theta_i\lambda_i}{\epsilon_{x_i}\theta_j\lambda_j} \tag{5}$$

Equation (5) is valid for small optical densities $(cd(\epsilon_{\parallel} - \epsilon_{\perp})) \ll 1$. An example of an absorption polarization spectrum and a circular dichroism spectrum is presented in Fig. 3. The absorption spectrum

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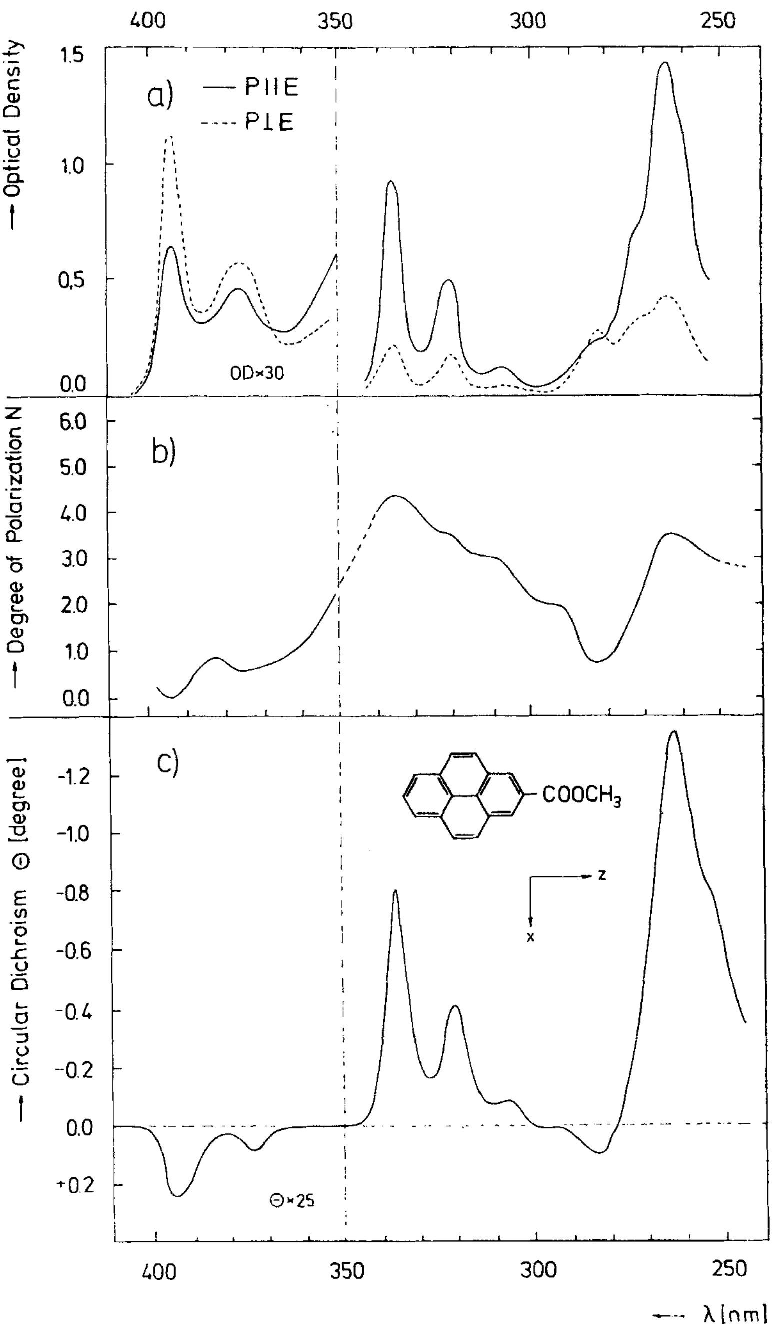
Figure 3. (a) Absorption polarization spectrum of pyrene-2-carbonic methyl ester (PCME). The spectrum was taken in an oriented 1.85 : 1 by weight mixture of cholesteryl chloride and cholesteryl laurate at the nematic temperature $T_{\text{nem}} \approx 30\,°\text{C}$. The spectrum $P \parallel E$ was taken with the linear polarizer P oriented parallel to the electric field E. The spectrum $P \perp E$ (broken curve) was taken with P oriented perpendicular to E. The concentrations were 10^{-3}m and 5.10^{-2}m. (b) Degree of polarization N defined by Eq. (2) as determined from the absorption polarization spectrum. Using Eq. (3) the following values of the order parameters have been determined: $S_{xx} = -0.162$; $S_{yy} = -0.354$ and $S_{zz} = +0.515$. (c) Circular dichroism spectrum of PCME dissolved in a cholesteric mixture of 55.5 mole percent cholesteryl nonanoate and 44.5% cholesteryl chloride taken at $T = 30\,°\text{C}$. The PCME concentration was $c = 5 \times 10^{-3}$ mole/liter, the solvent pitch was $\lambda_{\max} \approx 900\,\text{nm}$ and the sample thickness was $d = 20\,\mu\text{m}$. The baseline has been arbitrarily set to zero. The spectrum was taken with a Cary 60 spectropolarimeter as described earlier.(7)


400
350
300
250
→ Optical Density
1.5
1.0
0.5
0.0
a)
— P∥E
---- P⊥E
OD×30
→ Degree of Polarization N
6.0
5.0
4.0
3.0
2.0
1.0
0.0
b)
→ Circular Dichroism Θ [degree]
-1.2
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
+0.2
c)
COOCH$_3$
z
x
Θ×25
400
350
300
250
←-- λ [nm]

of pyrene-2-carbonic-methylester consists of 4 electronic transitions with 0–0-vibrational bands situated at 263 nm, 282 nm, 336 nm and 395 nm. It is found that the bands at 263 and 336 nm are polarized parallel to the long molecular (z-) axis whereas the bands at 282 and 395 nm are polarized parallel to the short in-plane (x-) axis. Fig. 3 also clearly shows that the circular dichroism changes the sign when the degree of polarization N changes from a value $N < 1$ to a value $N > 1$.(12)

4. Results and Comparison with Theory

The order parameters of a large number of aromatic molecules in a "compensated" nematic mixture of cholesteryl chloride and cholesteryl laurate (1.85 : 1 by weight) have been determined at $T = T_{\text{nem}} = 30\,^{\circ}\text{C}$ from linear dichroism measurements. The results are summarized in Table 1. In many cases the order parameters could only be determined for the long molecular axis. The molecules presented in Table 1 exhibit large differences in the molecular shape and in their physical properties. By analysing the data collected in Table 1 it is therefore possible to correlate the formally introduced order parameters of a molecule with its physical properties. As will be shown below such a correlation provides valuable information on the anisotropic solute–solvent interaction.

London dispersion forces and to a smaller extent repulsive forces play a dominant role in the anisotropic intermolecular interaction potential (cf. Refs. 13 and 14) and therefore we will try in the following to analyse the data of Table 1 in terms of these two interaction mechanisms. If the anisotropic solute–solvent interaction were determined mainly by repulsive forces, a correlation between the average orientation S_{zz} of the long molecular (z-) axis of an elongated molecule and its spatial dimensions would be expected.(13) In Fig. 4 we plotted the order parameters S_{zz} of a number of elongated aromatic molecules as function of the difference $2l_z - l_x - l_y$ where l_z, l_x and l_y are the Van der Waals dimensions of the solute molecules in the direction of the long axis, the short in plane axis and the axis in a direction perpendicular to the molecular plane, respectively. A number of molecules fulfill a linear relationship between S_{zz} and the above difference of the molecular dimensions. However,

TABLE 1 Values of the elements of the Saupe order matrix determined from the degree of polarization with Eq. (3). For the orientation of the axes x, y, and z in the solute molecule refer to Fig. 4 and Fig. 5.

Compound	S_{xx}	S_{yy}	S_{zz}	Structure
Coronene	0.172	0.172	−0.344	
Triphenylene	0.133	0.133	−0.266	
Benzene	0.040	0.04	−0.08	C_6H_6
Diethylaniline(4)	0.01	−0.198	0.188	$C_6H_5—N(C_2H_5)_2$
Azulene(5)	0.013	−0.233	0.22	$C_{10}H_8$
p-N,N-Dimethylamino-anisole	—	—	0.265	$CH_3O—C_6H_4—N(CH_3)_2$
Pyrene(6)	0.009	−0.279	0.27	$C_{16}H_{10}$
N,N,N′,N′-Tetramethyl-*p*-phenylenediamine(7)	−0.085	−0.218	0.303	$P—(CH_3)_2N—C_6H_4—N(CH_3)_2$
Anthracene(1)	−0.100	−0.233	0.33	$C_{14}H_{10}$
Perylene(19)	—	—	0.33	$C_{20}H_{12}$
1,2,4,5-Tetracyano-benzene(17)	−0.021	−0.329	0.35	$1,2,4,5\text{-}C_6H_2(CN)_4$
N,N-Dimethyl-*p*-Toluidine(18)	−0.115	−0.235	0.35	$CH_3—C_6H_4—N(CH_3)_2$
Biphenyl(10)	—	—	0.375	$H_5C_6—C_6H_5$
1,3,6,8-Tetrachloro-pyrene	−0.024	−0.364	0.388	$C_{16}H_6Cl_4$
trans-Azobenzene(15)	—	—	0.455	$H_5C_6—N{=}N—C_6H_5$
cis-Azobenzene(8)	—	—	0.32	$H_5C_6—N{=}N—C_6H_5$
Chrysene(14)	—	—	0.455	$C_{18}H_{12}$
p-Dicyanobenzene(21)	−0.11	−0.35	0.46	$CN—C_6H_4—CN$
Terphenyl(16)	—	—	0.48	$C_6H_5—C_6H_4—C_6H_5$
Tetracene(2)	−0.147	−0.339	0.485	$C_{18}H_{12}$
Pyrene-2-Carbonic Methyl Ester(13)	−0.162	−0.354	0.515	$C_{16}H_9—COOCH_3$

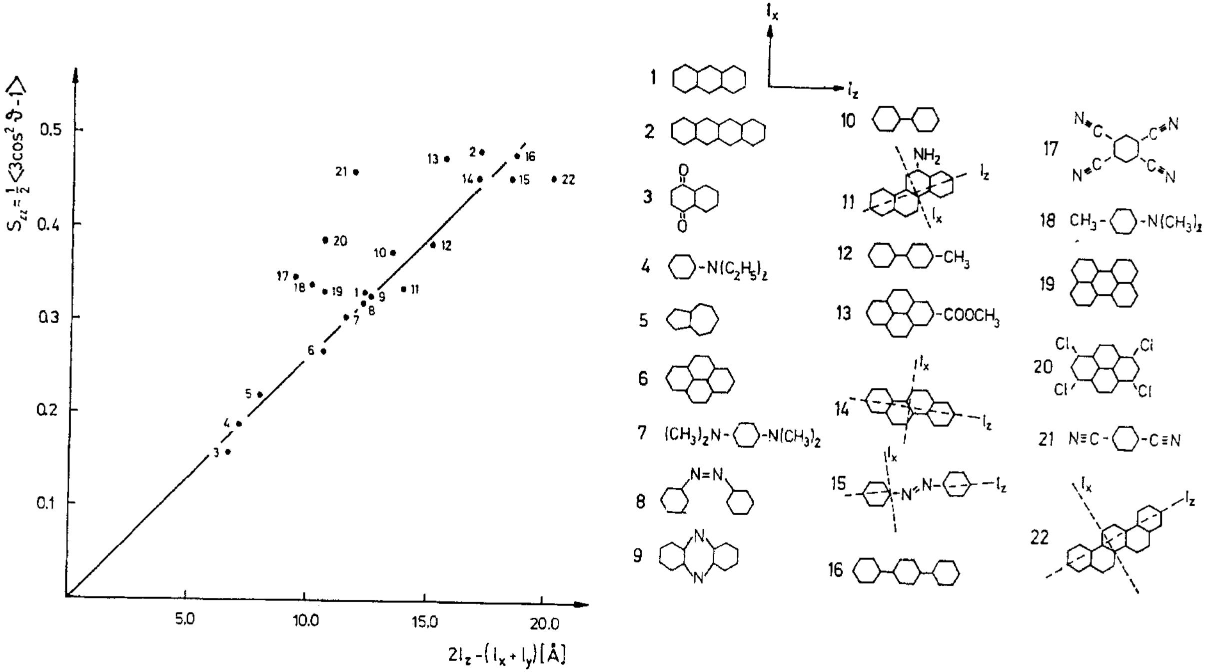


Figure 4. Relation between the average orientations S_{zz} (cf. Table 1.) of the long molecular axis (l_z) of elongated aromatic molecules and the difference $2l_z - l_x - l_y$ of the molecular dimensions in the direction of the x-, y-, and z-axis respectively. The solid straight line is given by the equation $S_{zz} = 0.262\ (2l_z - l_x - l_y)$. For asymmetric molecules the z-axis has been taken to be parallel to the longest molecular dimension. For the determination of S_{zz} we assumed that the transition with the largest value of N was polarized parallel to this axis.

large deviations from this linear relationship are obtained for molecules with highly polarizable substituents, e.g. CN or Cl.

These large deviations from the linear relationship indicate that anisotropic repulsive forces are not decisive for the anisotropic orientation distribution of aromatic solute molecules in liquid crystals. In order to analyse our data in terms of the anisotropic dispersion forces we calculated the solute–solvent interaction potential with the reaction field technique developed by Linder.⁽¹⁷⁾ As will be shown in the appendix the anisotropic dispersion interaction can be expressed in terms of the principal polarizabilities α_{xx}, α_{yy}, α_{zz} of the solute molecules by the following equation:

$$W^{an} = Q(\alpha_{xx}\sin^2\vartheta\cos^2\varphi + \alpha_{yy}\sin^2\vartheta\sin^2\varphi + \alpha_{zz}\cos^2\vartheta) \qquad (6)$$

where ϑ and φ denote the polar angles of the liquid crystal optical axis in the solute molecular coordinate system x, y, z.

With this anisotropic interaction potential the order parameter $S_{x_ix_i}(x_i \equiv x, y, z)$ of the solute molecules can now be calculated with the following equations.⁽¹¹,¹⁵⁾

$$S_{x_ix_i} = \int_0^\pi \int_0^{2\pi} f_{x_ix_i} \exp\{W^{an}/kT\} \sin\vartheta \, d\vartheta \, d\varphi \Big/ \int_0^\pi \int_0^{2\pi} \exp\{W^{an}/kT\} \sin d\vartheta \, d\varphi \qquad (7)$$

where $f_{xx} = \frac{1}{2}(3\sin^2\vartheta\cos^2\varphi - 1)$; $f_{yy} = \frac{1}{2}(3\sin^2\vartheta\sin^2\varphi - 1)$; $f_{zz} = \frac{1}{2}(3\cos^2\vartheta - 1)$.

In order to calculate order parameters with this equation, the coefficient Q and values of the principal solute polarizabilities must be known. For a number of unsubstituted aromatic molecules values of the principal polarizabilities habe been determined by Kerr-effect measurements⁽¹⁸,¹⁹⁾ or are known from theoretical work.⁽²⁰⁾ The discussion of the general equation for the dispersion interaction potential derived in the appendix strongly suggests that the coefficient Q does not depend appreciably on the physical nature of the solute molecules. We therefore calculated the order parameters S_{xx}, S_{yy} and S_{zz} of several unsubstituted aromatic molecules with known values of the principal polarizabilities by adopting a constant value of Q for all solute molecules and order parameters. By fitting the calculated and the experimental values of the order parameter S_{zz} for anthracene a value of $Q/kT = 0.115$ [Å^{-3}] has been obtained.

With this value of Q we calculated the order parameters S_{xx}, S_{yy} and S_{zz} for several unsubstituted aromatic molecules.†

The results are presented in Fig. 5 and in Table 2. The solid curve in Fig. 5 has been calculated with Eq. (7) by varying the difference $\Delta\alpha = (2\alpha_{zz} - \alpha_{xx} - \alpha_{yy})$, while the experimental values of S_{zz}, given by the dots, have been plotted as function of the difference $\Delta\alpha$ calculated with the values of the principal polarizabilities summarized in Table 2. Excellent agreement between calculated and experimental order parameters S_{zz} is obtained. For small values of the solute order a linear relationship between S_{zz} and the difference $\Delta\alpha$ holds, which has already been reported in a preliminary publication.(5)

The excellent agreement between theoretical and empirical values of the order parameters can be most clearly seen in Table 2. where we present calculated and experimental values of all three order matrix elements S_{xx}, S_{yy} and S_{zz}.

The results of Fig. 5 and Table 2 provide evidence (1) that the dispersion interaction potential calculated in the appendix yields the correct dependence of W^{an} on the solute orientation although the absolute value of W^{an} is by an order of magnitude too small and (2) that the principal polarizabilities of aromatic molecules can be determined with good accuracy from their average orientation in liquid crystals.

5. Discussion and Conclusion

The experimental order parameters of unsubstitutes aromatic molecules could be explained quantitatively by assuming that the anisotropic solute–solvent interaction is determined by London dispersion forces alone. This seems to be in contrast with the results obtained by Luckhurst *et al.* for cholestane spin probes dissolved in nematic solvents of azoxy compounds.(16) These authors concluded from the temperature dependence of the solute order that the anisotropic pseudo-potential for these spin probes must include interactions in addition to the London dispersion forces. It is

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†The integrations in Eq. (7) have been performed with an Univac 1108 computer by the Gesellschaft für Datenverarbeitung mbH, Göttingen.

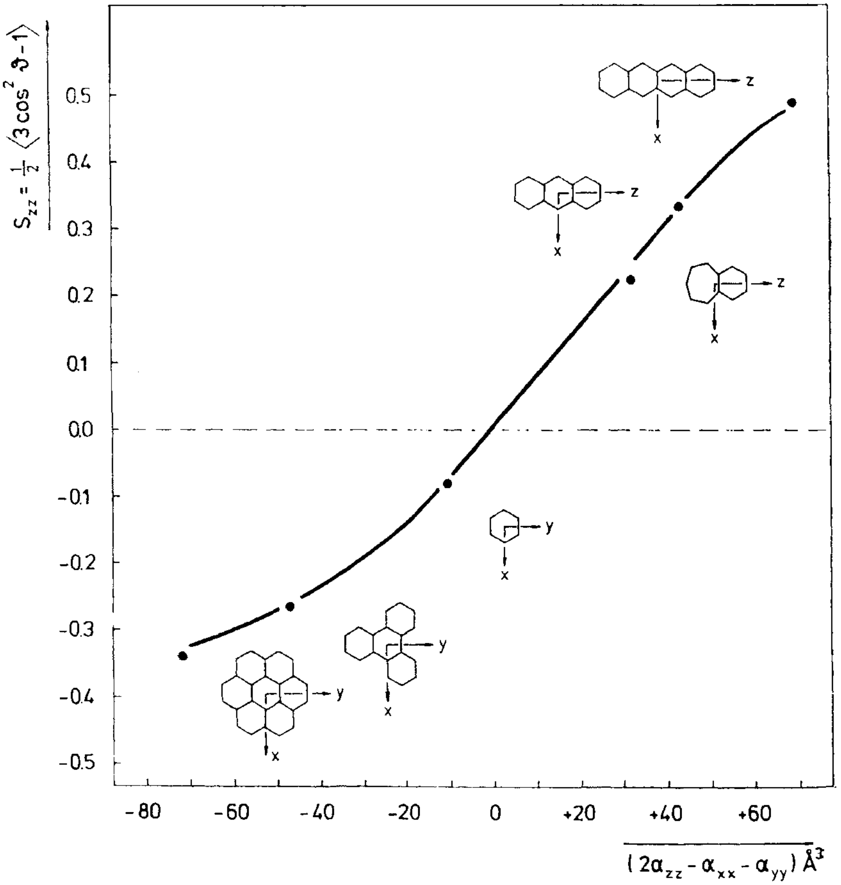

Figure 5. Relation between the average orientation S_{zz} of several aromatic molecules in a "compensated" nematic mixture and the anisotropy of the polarizabilities of these molecules. ϑ is the angle between the z-axis of the solute molecule and the optical axis of the liquid crystal. The dots are experimental values determined in a 1.85 : 1 by weight mixture of cholesteryl chloride and cholesteryl laurate, while the difference $\Delta\alpha = 2\alpha_{zz} - \alpha_{xx} - \alpha_{yy}$ has been determined with the values of the principal polarizabilities given in Table 2. The drawn curve has been calculated with Eq. (7) using a value of $Q/kT = 0.115$ Å^{-3}. This value has been obtained by fitting the experimental and the theoretical value of S_{zz} for anthracene.

TABLE 2 Comparison of calculated and experimental values of all three order parameters of unsubstituted aromatic molecules. In the case of elongated molecules the z-axis is taken parallel to the long molecular axis and the y-axis is perpendicular to the molecular plane. For molecules with C_{6h} symmetry the z-axis is directed perpendicular to the molecular plane. The values of the principal polarizabilities (given in Å^3) are (a) experimental values from Kerr-effect measurements(18,19) and (b) theoretical values from Amos *et al.*(20) All order parameters have been calculated with value $Q/kT = 0.115$ Å^{-3}.

	Experimental values			Theoretical values						
Molecules	S_{xx}	S_{yy}	S_{zz}	S_{xx}	S_{yy}	S_{zz}	α_{xx}	α_{yy}	α_{zz}	**x**[Å^3]
Benzene	0.04	0.04	−0.08	0.037	0.037	−0.075	11.2	11.2	6 0^a	9 5
Triphenylene	0 133	0.133	−0.266	0.129	0.129	−0.258	39.0	39.0	15.5^a	31.3
Coronene	0.172	0.172	−0.344	0.162	0.162	−0.325	57.0	57.0	21.0^a	45.0
Azulene	0.013	−0.233	0.22	−0.017	−0.229	0.246	23.2	8.7	31.8^b	21.2
Anthracene	−0.100	−0.23	0.33	−0.083	−0.253	0.336	26.0	12.0	40.2^a	26.0
Tetracene	−0.145	−0.34	0.49	−0.120	−0.356	0.476	46.3	13.5	64.5^b	41.4

reasonable to assume that these additional interaction terms are mainly connected with repulsive forces. Measurements of the temperature dependence of the solute order parameters in the "compensated" mixtures used in this work are hampered by the fact that the composition of the solvent has to be varied slightly with the temperature. Temperature dependent measurements have therefore not yet been performed and we therefore cannot exclude small additional terms. Our results presented above lead us to the conclusion that the average orientation distribution of aromatic molecules is determined primarily by London dispersion forces. This conclusion† is in accordance with the results obtained by Nehring *et al.*(21) and by Robertson *et al.*(22) for substituted benzenes.

Unsubstituted aromatic molecules satisfy a linear relationship between the order parameter S_{zz} and the difference of the molecular dimensions to a very good degree of accuracy (cf. Fig. 4). However, this is due to the fact that for these molecules $2l_z - l_x - l_y$ is proportional to the difference ($\Delta\alpha$) of the principal polarizabilities as can be easily verified with the results of Fig. 4. and Table 2. The linear relationship between the average orientation and the molecular dimensions is therefore a direct consequence of the proportionality between S_{zz} and $\Delta\alpha$. For molecules with highly polarizable unsaturated substituents (e.g. CN-groups) a proportionality between the differences of the molecular dimensions and the principal polarizabilities cannot be expected due to strong mesomeric interactions between the π electrons of the substituent and the aromatic ring.

Appendix

CALCULATIONS OF THE ANISOTROPIC INTERACTION POTENTIAL(23)

The reaction field approach of the intermolecular interaction potential is based on the following model:

The fluctuating electric moment $\mathbf{M}(t)$ of a solute molecule l induces

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†This conclusion is further supported by results obtained for charge transfer complexes between aromatic molecules.(6) These sandwiched complexes which are rather spherical in shape orient excellently with their common plane parallel to the optical axis of the liquid crystal. It is obvious that the polarizability in any direction parallel to the plane of such complexes is much larger than in a direction perpendicular to the plane.

a moment $\mathbf{M}_s(t)$ in the surrounding solvent molecules s. The "reaction" field emanating from these moments $\mathbf{M}_s(t)$ in turn interacts with the moment $\mathbf{M}_l(t)$ of the solute. The reaction field approach is a macroscopic theory which considers the neighbourhood of a solute molecule as a continuum, and therefore short range effects are neglected. The total "reaction" field at the site of the solute molecule is given by the following sum which extends over all solvent molecules.

$$\mathbf{R}_{ls} = \sum_s \mathbf{T}_{sl} \cdot \mathbf{X}_s \cdot \mathbf{T}_{ls} \cdot \mathbf{M}_l \tag{A.1}$$

$\mathbf{T}_{ls}$ is a tensor of dyadic form

$$\mathbf{T}_{ls} = \frac{1}{r_{ls}{}^3}\left\{\mathbf{E} - \frac{3r_{ls} \cdot r_{ls}}{r_{ls}{}^2}\right\} \tag{A.2}$$

and $\mathbf{X}_s$ is the susceptibility tensor of the solvent. The total interaction energy is the given by

$$W_{ls} = -\tfrac{1}{2}\mathbf{M}_l \cdot \mathbf{R}_{ls} \tag{A.3}$$

The interaction potential between the fluctuating moments $\mu_s(t)$ and $\mu_l(t)$ has been calculated by applying the equations given by Linder⁽¹⁷⁾ for the isotropic case to each term occurring in the tensor product of Eq. (A.1), while the sum over s has been replaced in the usual way by averaging the interaction potential over all molecular orientations and over all distances of the solvent molecules from the site of a solute molecule.

In our approach we made the following simplifying assumptions:

1) The solute molecules are situated in spherically shaped solvent holes and the spatial distribution of the solvent molecules about this hole is isotropic.

2) The rotational and translational motion of the molecules are decoupled and therefore the average over these molecular motions can be carried out separately (cf. Ref. 25).

3) The solvent order is not influenced by the solute. This condition is fulfilled in the optical experiments where low solite concentrations ($c \leqslant 10^{-3}$ mol/liter) are used.

With these assumptions we calculated the following equation for the solute–solvent dispersion interaction energy:⁽²³⁾†

$$W_{ls} = -\frac{\pi^2 I_l \cdot I_s N_L}{90(I_l + I_s)} \frac{1}{V_l V_s} \Big\{ \vartheta\, 30 \bar{X} \bar{\alpha} - (X_{\parallel} - X_{\perp}) \bar{\alpha} S_s + (X_{\parallel} - X_{\perp}) S_s \times [\alpha_{xx} \sin^2\vartheta \cos^2\varphi + \alpha_{yy} \sin^2\vartheta \sin^2\varphi + \alpha_{zz} \cos^2\vartheta] \Big\} \qquad (A.4)$$

In this equation $\bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$ and $\bar{X} = \frac{1}{3}(X_{\parallel} + 2X_{\perp})$, where α_{xx}, α_{yy}, α_{zz} are the principal polarizabilities of the solute molecules and $X_{\parallel}$ and $X_{\perp}$ denote the dielectric susceptibilities of the liquid crystal matrix in a direction parallel and perpendicular to the optical axis. ϑ and φ denote the polar angles of the liquid crystal optical axis in the solute fixed axis system x, y, z. I_l and I_s are the ionization potentials of the solute and the solvent molecules, respectively, and S_s denotes the solvent order. V_l and V_s are the molar volumes of the solute and the solvent, respectively. The above equation is analogous to the relations derived by Maier and Saupe⁽²⁵⁾ and by Kaplan *et al.*⁽²⁴⁾ for the solvent–solvent interaction.

In the course of the derivation of Eq. (A.4) Kirkwood's⁽²⁶⁾ procedure for the calculation of the ensemble average of the product $\mathbf{T}_{ls}\mathbf{T}_{sl}$ has been adopted, while assuming that the spatial distribution of the solvent molecules is determined by a hard core potential. The coefficient before the bracket { } contains additional terms if attractive forces are considered, which do not, however, alter the orientation dependent part of Eq. (A.4).

According to Eq. (A.4) the coefficient Q of Eq. (6) depends on the nature of the solute through the ionization potential I_l and the molar volume V_l. Since the ionization potentials of aromatic molecules range from about 7 eV (tetracene) to 9.2 eV (benzene), an average value of $I_l = 8$ eV can be assumed for all solute molecules. It is further reasonable to assume that the size of the solvent cavity formed around the solute molecule is mainly determined by the shape of the solvent molecules. The product $V_l V_s$ in Eq. (A.4) can therefore be replaced by the square of the molar volume of the solvent. This assumption has also been adopted recently by Luckhurst *et al.*⁽¹⁶⁾

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†The coefficient in the equation for the anisotropic part of the interaction potential reported in a previous short communication⁽⁵⁾ is too large by factor of 10.

By inserting numerical values for the physical parameters in Eq. (A.4) we estimated the anisotropic interaction potential for anthracene as solute and the "compensated" nematic mixtures and azoxyanisole, respectively, as solvent. The interaction potential differences for parallel and perpendicular orientation of the long molecular axis are $\Delta W_{ls} \sim 0.0015$ eV and $\Delta W_{ls} \sim 0.004$ eV for the cholesteryl derivatives and azoxyanisole, respectively. These values are much smaller than the thermal energy of 0.025 eV at 25 °C and an appreciable solute orientation would not be expected from our approximation. However, judged from our results presented above it is reasonable to assume that a more exact calculation does not affect the orientation dependent part of Eq. (A.4) and our conclusion that the coefficient in front of the bracket { } in Eq. (A.4) does not depend on the nature of the solute, remains valid.

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