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W. Haase [a] & H. Wedel [a]

[a] Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstrasse 20, D-6100, Darmstadt, Federal Republic of Germany

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The Application of Nematic Liquid Crystals as Anisotropic Solvents in the Optical Absorption Spectroscopy for the Determination of the Polarization of Electronic Transitions of Organic Molecules and Cu(II)—Complexes

W. HAASE and H. WEDEL

Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstrasse 20, D-6100 Darmstadt, Federal Republic of Germany

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Nematic liquid crystals are well suited as anisotropic solvents in the optical absorption spectroscopy. They make it possible to determine the band polarizations of solute molecules by linear dichroism measurements. With homogeneously aligned nematic phases the investigation can be performed by polarized light, with homeotropic layers by natural light. With the nematic phases used (N9, ZLI 612/Merck) a wavelength range down to c. 325 nm can be achieved.

The dichroic ratios $R = D_{\parallel}/D_{\perp}$ and $R' = D_{\mathrm{iso}}/D_{\perp}$ have to be corrected by multiplication with the ratio of the refractive indices $n_{\parallel}(\lambda)/n_{\perp}(\lambda)$ and $n_{\mathrm{iso}}(\lambda)/n_{\perp}(\lambda)$ respectively. Therefore the wavelength dependence of the refractive indices has been determined.

1 INTRODUCTION

In order to determine the transition dipole moment in the molecular framework, band polarizations and intensities have to be measured. The experimental determination of the band polarization requires samples with at least partially oriented molecules. It is often very difficult to get pure or dotted single crystals[1,2] suited for spectroscopy. Therefore in the last years methods were developed by which the orientation of the molecules is achieved in noncrystalline hosts. The most important ones are the photoselection technique,[1,3–5] the electrochromism,[6–10] the spectroscopy in stretched polymer sheets,[11–17] and in nematic liquid crystals.

Nematic liquid crystals can be aligned relatively simple homogeneously or homeotropically and then behave like uniaxial crystals. Because of the guest-host-effect[18,19] they are well suited as anisotropic solvents in the spectroscopy for the determination of anisotropic molecular properties.

Nematic and compensated nematic phases can be aligned in the same way. Therefore both types of liquid crystals can be used. There has been a number of investigations in the NMR-,[18,20,21] the EPR-,[20,22–24] the IR-[25–28] and the electronic spectroscopy in the UV/VIS. In this field nematic[19,26,29–33] and compensated nematic phases[34–41] have been used. In the latter type of solvents it is possible to perform fluorescence polarization[37,39,41] and circular dichroism[37,42–44] measurements. The present work deals with the measurement of the absorption polarization spectra in the UV/VIS with nematic phases as orientation matrices.

2 PRINCIPLE OF THE MEASUREMENTS

The transition probability and therefore the intensity of a band in the absorption spectrum is proportional to the projection of the transition dipole moment on the electric vector of the light. This statement is valid for electric dipole transitions. If the orientation of the molecules and the electric vector is known, informations about the transition moment can be derived from the measured relative band intensities. Solute molecules are aligned in liquid crystals with the axis of the highest molecular polarizability—in most cases the long molecular axis—preferably parallel to the optical axis of the liquid crystalline solvent.[32,37,38] Nematic liquid crystals can easily be aligned uniaxially. Therefore they are well suited as solvents for linear dichroism measurements.

2.1 Measurements with polarized light

In most cases the nematic layers are oriented homogeneously with the optical axis parallel to the walls of the cell. Two spectra have to be recorded, one with the electric vector parallel, the other with the electric vector perpendicular to the optical axis. Now the dichroic ratio R (for the i-th transition) is defined:

$$R_i = \frac{D_{i,\parallel}}{D_{i,\perp}} = \frac{\varepsilon_{i,\parallel} \cdot c \cdot d}{\varepsilon_{i,\perp} \cdot c \cdot d} = \frac{\varepsilon_{i,\mathrm{iso}} + \frac{2}{3}(\varepsilon_{i,x} S_{xx} + \varepsilon_{i,y} S_{yy} + \varepsilon_{i,z} S_{zz})}{\varepsilon_{i,\mathrm{iso}} - \frac{1}{3}(\varepsilon_{i,x} S_{xx} + \varepsilon_{i,y} S_{yy} + \varepsilon_{i,z} S_{zz})}. \qquad (1)$$

(D_i = optical density, ε_i = extinction coefficient, c = concentration,
d = cell thickness, S_{jj} = diagonal element of the Saupe order matrix.)

Without additional information, R yields the relative band polarization. If $R > 1$, the largest component of the transition moment is directed parallel or if $R < 1$, it is directed perpendicular to the long molecular axis. For molecules with e.g. D_{2h} or C_{2v}-symmetry the transition moments have only one component parallel to a molecular axis of symmetry. In such cases it is possible to get information about the absolute polarization. If the band polarization is known, it is possible to derive the related diagonal element of the Saupe order matrix for the solute molecule:

$$S_{jj} = \frac{R_i - 1}{R_i + 2}. \tag{2}$$

$(j = x, y, \text{or } z)$.

2.2 Measurements without polarized light

1973 it was shown by Kelker *et al.*[28] that it is possible to measure the IR-dichroism without polarized light. We have applied this method to the investigation of electronic transitions.[33]

If the light is sent through a homeotropic layer parallel to the optical axis, the electric vector is directed definitely perpendicular to the long molecular axes, because it vibrates perpendicular to the direction of propagation. So it is possible to measure $D_\perp$ without polarized light. Then the alignment of the sample is destroyed by heating it above the clearing point and the spectrum of the isotropic solution is measured. In analogy to (1) a dichroic ratio R' is defined

$$R'_i = \frac{D_{i,\text{iso}}}{D_{i,\perp}} = \frac{\varepsilon_{i,\text{iso}} \cdot c_2 \cdot d_2}{\varepsilon_{i,\perp} \cdot c_1 \cdot d_1}. \tag{3}$$

(The indices 1 and 2 relate to the fact, that changes of concentration and possibly of the cell thickness between the two temperatures may occur.) Because of (1) the following equations hold:

$$D_{\text{iso}} = D_\perp + \tfrac{1}{3}(D_\parallel - D_\perp) \tag{4a}$$

and

$$R' = \tfrac{2}{3} + \tfrac{1}{3}R. \tag{4b}$$

Therefore $R \gtrless 1$ implies that $R' \gtrless 1$ and

$$S_{jj} = \frac{R'_i - 1}{R'_i}. \tag{5}$$

If the solute molecules are stable, when heating the solution above the clearing point, the method yields the same information as the experiments with polarized light.

2.3 Correction of the spectra for the solvent birefringence

If the birefringence of the nematic solvents cannot be neglected, the dichroic ratios have to be corrected[32,33]

$$R_{i,\mathrm{corr}} = \frac{D_{i,\parallel} \cdot n_{\parallel}(\lambda)}{D_{i,\perp} \cdot n_{\perp}(\lambda)} \tag{6a}$$

$$R'_{i,\mathrm{corr}} = \frac{D_{i,\mathrm{iso}} \cdot n_{\mathrm{iso}}(\lambda)}{D_{i,\perp} \cdot n_{\perp}(\lambda)} \tag{6b}$$

In the visible range the dispersion curves $n_i(\lambda)$ can be determined with the help of the prism method[45,46] and over a wide frequency range by an interferometric method.[32,47–49]

If monochromatic light is sent through an experimental setup consisting of a cell with strictly parallel glass or quartz plates placed between two linear polarizers directed parallel to each other, the transmitted light is modulated caused by interference. The condition for a maximum is

$$\frac{2 \cdot n(\lambda) \cdot d}{\lambda_k} = k \qquad k = 1, 2, \ldots \tag{7a}$$

$n(\lambda)$ is the wavelength dependent refractive index of the medium with which the cell is filled. If it is filled with a homogeneously aligned liquid crystal, $n_{\parallel}(\lambda)$ and $n_{\perp}(\lambda)$ can be determined with the polarization direction parallel or perpendicular to the optical axis. On condition that the electric vector of the light and the optical axis include an angle of 45°, it is possible to determine $\Delta n(\lambda)$. Then the following equation holds:

$$\frac{\Delta n(\lambda) \cdot d}{\lambda_k} = k \qquad k = 1, 2, \ldots \tag{7b}$$

For the empty cell over the whole wavelength range $n(\lambda)$ nearly equals 1. Then it is possible to determine the cell thickness. Taking two neighbouring maxima at λ and λ', the order of interference k can be eliminated:

$$d = \frac{\lambda\lambda'}{2(\lambda - \lambda')} \tag{8}$$

It is not allowed to use the analogous equations for the determination of the refractive indices or the birefringence:

$$n(\lambda) = \frac{\lambda\lambda'}{2d(\lambda - \lambda')} \tag{9a}$$

$$\Delta n(\lambda) = \frac{\lambda\lambda'}{d(\lambda - \lambda')} \tag{9b}$$

The approach $n(\lambda) = n(\lambda')(\Delta n(\lambda) = \Delta n(\lambda'))$ causes to high values of $n(\lambda)(\Delta n(\lambda))$, especially at small wavelengths. Therefore equations (7a) and (7b) have to be used.

2.4 Separation of overlapping spectral bands

The dichroic ratio does not yield definite informations, if the absorption spectrum contains overlapping bands or bands with vibronic structures. Liquid crystalline films are always oriented uncompletely. Therefore $D_{\parallel}$ partially contains $D_{\perp}$ and vice versa. A reduction procedure developed for the spectroscopy in stretched polymer sheets[13–17] enables us to calculate the spectra of completely aligned samples, and often the overlapping bands can be separated into components.

We have applied this method to measurements in nematic liquid crystals.[33] This is possible because both spectroscopic techniques are based on the alignment of the molecules in uniaxial hosts. Therefore the same orientation model is valid.

The reduced spectra are calculated from the (corrected, vid. 2.3) experimental curves with the help of the reduction factors $r_{\parallel}$ and $r_{\perp}$

$$D_{\parallel,\text{red}} = D_{\parallel,\text{exp}} - r_{\parallel} \cdot D_{\perp,\text{exp}} \tag{10a}$$

$$D_{\perp,\text{red}} = D_{\perp,\text{exp}} - r_{\perp} \cdot D_{\parallel,\text{exp}} \tag{10b}$$

Possibly $D_{\perp,\text{red}}$ has to be multiplied with a normalization factor f. If the host is aligned perfectly uniaxial, f can be calculated from $r_{\parallel}$ and $r_{\perp}$

$$f = \frac{r_{\parallel} + 2}{2r_{\perp} + 1}. \tag{11}$$

3 EXPERIMENTAL TECHNIQUES

The experimental cells for both methods described are mounted from quartz-plates, coated with transparent and electrically conducting SnO_2. Two strips of 25 μm thick Hostaphan are used as spacers. The cells can be filled from the open sides by capillary forces. The experimental setup is thermostated within less than ±0.5°C.

For the measurements with polarized light, the *homogeneous alignment* of the nematic layer is achieved with liquid crystals with negative dielectric anisotropy by applying an AC electric field of 6 kHz (in order to avoid electro-hydrodynamic effects) and by rubbing the quartzplates before mounting the cell. The electric field diminishes the straylight and enhances the completeness of the alignment. For the measurements of the present work N9 (Merck) was used, a mixture of nematic esters (mp: −20°C, clp: +60°C, $\Delta\varepsilon_{25^\circ\mathrm{C}}^{1\mathrm{kHz}}$: −0.5), and MBBA (mp: +21°C, clp: +45°C, $\Delta\varepsilon_{25^\circ\mathrm{C}}^{1\mathrm{kHz}}$: −0.6).

In general it is believed that nematic layers can be oriented by a rubbing procedure only up to 100 μm thickness. By combining the rubbing with the electric field, alignment could be achieved up to 500 μm thickness. So it is possible to perform measurements of bands with small intensity and of substances with small solubility. For these cells a teflon spacer was used.

For the measurements without polarized light the *homeotropic alignment* is achieved with nematic phases of positive dielectric anisotropy in a homogeneous electric field. Now it is not necessary to rub the quartzplates, because the orientation parallel to the electric field is definite. For the measurements of the present work ZLI 612 (Merck) was used, a mixture of nematic esters (mp: <0°C, clp: 46°C, $\Delta\varepsilon_{25^\circ\mathrm{C}}^{1\mathrm{kHz}}$: +0.6).

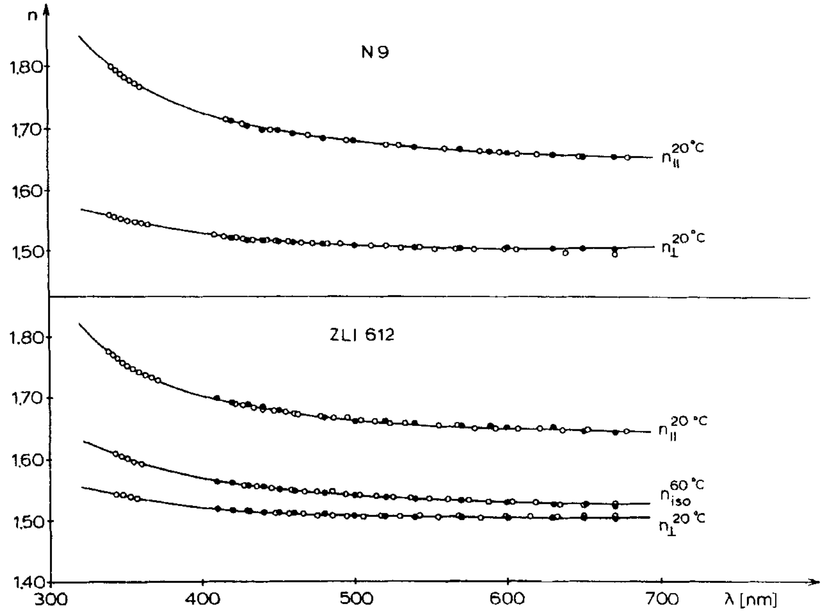


FIGURE 1 Dispersion of the refractive indices of N9 and ZLI 612. ● determined by the prism method; ○ interferometric values.

Both mixtures of esters are transparent down to c. 325 nm. The spectra of the oriented samples have been recorded at 20°C, and in the isotropic ZLI 612 at 60°C. The difference of the concentrations has been taken into account with $c_1 = 1.027 \cdot c_2$, the cell thickness was supposed as constant. The investigations have been carried out in a Cary 17 spectrophotometer which for the measurements with polarized light was equipped with polarizing filters KS DM (Käsemann). The measurements have been corrected for the contribution of the solvents and the self polarization of the apparatus by baseline subtraction.[39] The optical densities have been taken directly from the spectra without bandanalysis after refractive index correction. The plots of the spectra in N9 have been corrected by multiplying the optical densities with the related refractive indices. Because of the small difference of $n_{\mathrm{iso}}^{60^\circ\mathrm{C}}(\lambda) - n_{\perp}^{20^\circ\mathrm{C}}(\lambda)$ in ZLI 612 (0.02 to 0.07 over the whole investigated wavelength range) the experimental values of the spectra in ZLI 612 have been plotted.

The dispersion curves of the refractive indices for N9 and ZLI 612 have been measured by the prism and the interference method (Figure 1). The values for MBBA have been determined by the prism method and taken from literature.[46]

4 EXAMPLES OF APPLICATION

Table I shows the substances under investigation, the dichroic ratios, the order parameters if possible, and the difference in % between the corrected and uncorrected values. One can see that the correction cannot be neglected especially if Δn is relatively large. Even in cases of small Δn the error in the order parameter can be large if R is close to one and S_{jj} therefore is small (e.g. anthracene). Then even the birefringence of the compensated nematic mixtures cannot be neglected, because it can reach a value of 0.06 to 0.07.[50]

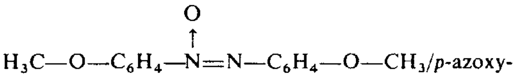
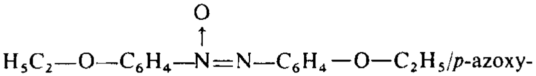
Figure 2a shows the polarized absorption spectra of cyclohexanone-4-nitrophenylhydrazone in N9. The example demonstrates that the reduction procedure described in section 2.4 is very powerful. The electronic spectrum in the wavelength range down to 325 nm (beginning of the solvent absorption) exhibits an intense strongly dichroic long axis polarized band at c. 360 nm with a shoulder centered around 430 nm with similar intensity for both polarizations. In the reduced spectra (Figure 2b) both transitions are perfectly separated and show different polarization.

Table I shows that the order parameters of the solute molecules depend on the molecular structure.

As expected S_{zz} is larger for PAP than for PAA because the anisotropy of the molecular polarizability increases due to substitution. The same is to be

TABLE I

Dichroic ratios and order parameters of the investigated substances

Compound	Solvent	λ(nm)[a]	R/R'	R'_{corr}/R_{corr}	Δ(%)[b]	S_{jj}	$S_{jj,corr}$	Δ(%)[b]	j[c]
anthracene	N9	381	0.544	0.618	13.6	−0.18	−0.15	16.7	x
	ZLI 612	380	0.848	0.871	2.7	−0.18	−0.15	16.7	
9.10-dibromoanthracene	N9	407	1.055	1.191	12.9	0.02	0.06	200	x
9.10-diphenylanthracene	N9	396	2.627	2.970	13.1	0.35	0.40	14.3	x
	ZLI 612	396	1.429	1.474	3.2	0.30	0.32	6.7	
$C_6H_5{-}N{=}N{-}C_6H_5$/azobenzene	N9	450	2.753	3.085	12.0	0.37	0.42	13.5	z
$(CH_3)_2N{-}C_6H_4{-}N{=}N{-}C_6H_4{-}N(CH_3)_2$/4,4′-dimethylaminoazobenzene	N9	485	7.844	8.739	11.4	0.70	0.72	2.9	z
	MBBA	485	3.744	4.328	15.6	0.48	0.53	10.4	
$(C_2H_5)_2N{-}C_6H_4{-}N{=}N{-}C_6H_4{-}N(C_2H_5)_2$/4,4′-diethylaminoazobenzene	N9	490	6.014	6.695	11.3	0.63	0.65	3.2	z
 $H_3C{-}O{-}C_6H_4{-}\overset{\overset{O}{\uparrow}}{N}{=}N{-}C_6H_4{-}O{-}CH_3$/*p*-azoxyanisole (PAA)	N9	360	6.059	6.933	14.4	0.63	0.66	4.8	z
	ZLI 612	360	2.261	2.348	3.9	0.56	0.57	1.8	
 $H_5C_2{-}O{-}C_6H_4{-}\overset{\overset{O}{\uparrow}}{N}{=}N{-}C_6H_4{-}O{-}C_2H_5$/*p*-azoxyphenetole (PAP)	N9	365	6.938	7.944	14.5	0.66	0.70	6.1	z
	ZLI 612	360	2.751	2.858	3.9	0.64	0.65	1.6	
$ON{-}C_6H_4{-}N(C_2H_5)_2$/4-nitroso-*N*,*N*′-diethylaniline	N9	420	2.314	2.604	12.5	0.31	0.35	12.9	z
$O_2N{-}C_6H_4{-}N{-}N{=}(C_6H_{10})$/cyclohexanone-4-nitrophenylhydrazone	N9	370	2.412	2.751	14.1	0.32	0.37	15.6	z
crysene	N9	325	2.006	2.341	16.7				
pyrene	N9	338	2.026	2.364	16.7	0.25	0.31	24.0	z
β-carotin	N9	520	6.827	7.675	12.4	0.66	0.69	4.6	z
	ZLI 612	520	2.378	2.442	2.7	0.58	0.59	1.7	
Bromo(2-diethylaminoethanolato)-Cu(II)	N9	408	1.365	1.550	13.5				
		675	1.144	1.259	10.1				
	ZLI 612	408	1.234	1.265	2.5				

[a] The wavelengths are taken where R has the highest value (not always the absorption maximum).

[b] The values of Δ(%) relate to the uncorrected dichroic ratios and order parameters respectively.

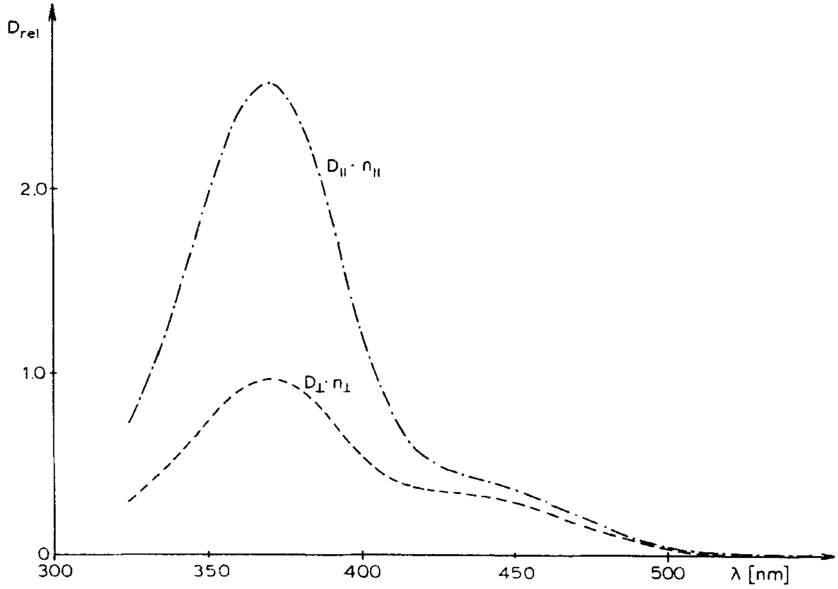


FIGURE 2a Absorption polarization spectra of cyclohexanone-4-nitrophenylhydrazone in N9.

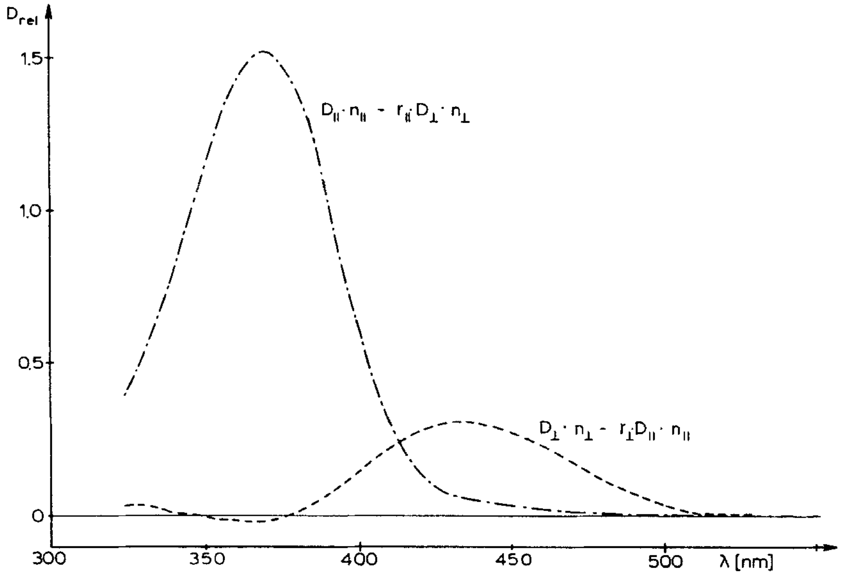


FIGURE 2b Reduced spectra of cyclohexanone-4-nitrophenylhydrazone.

observed in the comparison of azobenzene and 4,4'-bis-dimethylaminoazobenzene. But S_{zz} for the analogeous ethyl compound is smaller than for the methylcompound. Obviously in this case the ethylgroup contributes more to the polarizability parallel to a short axis than to the long molecular axis.

A good example for the influence of substituents on the orientation of solute molecules in the nematic solvent is the series anthracene, 9.10-dibromoanthracene, 9.10-diphenylanthracene. The spectra of these compounds are shown in Figures 3a–c. Anthracene is investigated extensively and already has been measured in liquid crystals.[29,33,39] The spectra of the other two compounds are analogous to that of anthracene and it can be believed that the band polarization is not influenced by the symmetric substitution.[51] The peak at the highest wavelength is interpreted as 0-0-transition polarized exactly parallel to the molecular x-axis (D_{2h}-symmetry). The measurements show that there is a different orientation of the molecules in the sequence anthracene, 9.10-dibromoanthracene, 9.10-diphenylanthracene.[51]

Anthracene is aligned with its molecule fixed z-axis preferably parallel, 9.10-diphenylanthracene preferentially perpendicular to the optical axis of the nematic layer. Based on the fact that for 9.10-dibromoanthracene the optical densities $D_{\parallel}$ and $D_{\perp}$ are nearly equal, it can be concluded that there is no large difference between the main polarizabilities α_{xx} and α_{zz}. Therefore

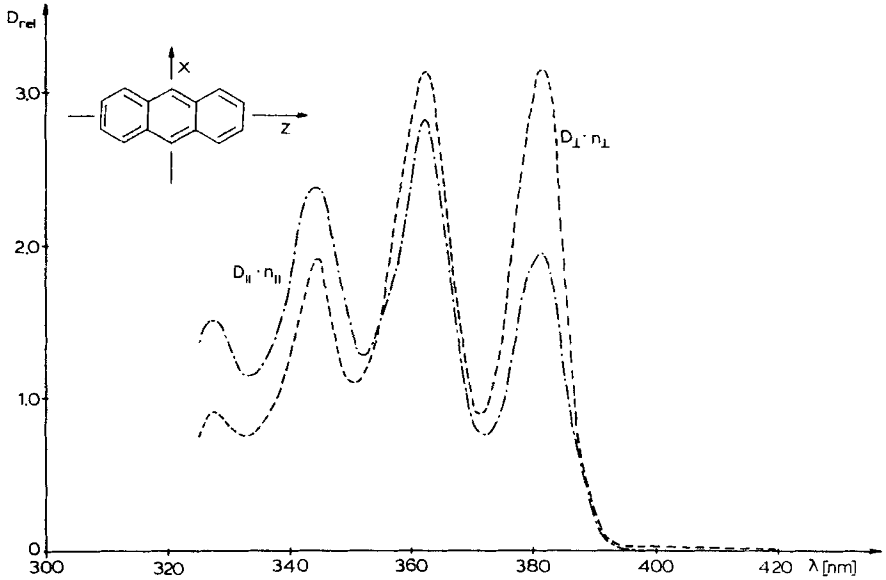


FIGURE 3a Spectra of anthracene in N9.

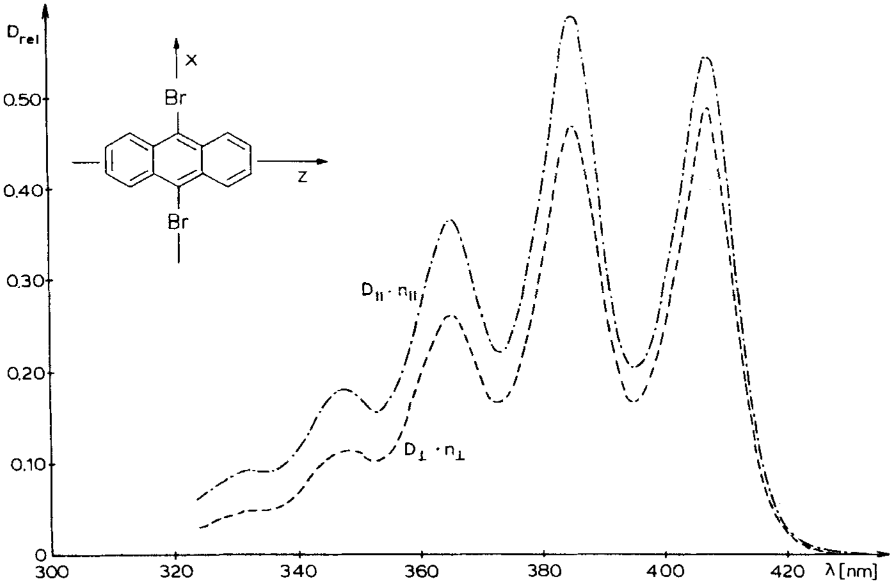


FIGURE 3b Spectra of 9.10-dibromoanthracene in N9.

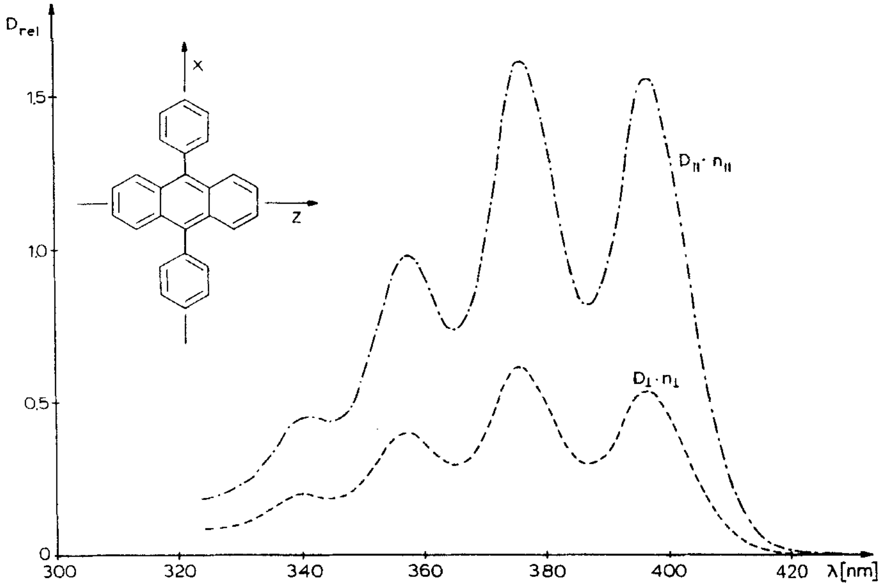


FIGURE 3c Spectra of 9.10-diphenylanthracene in N9.

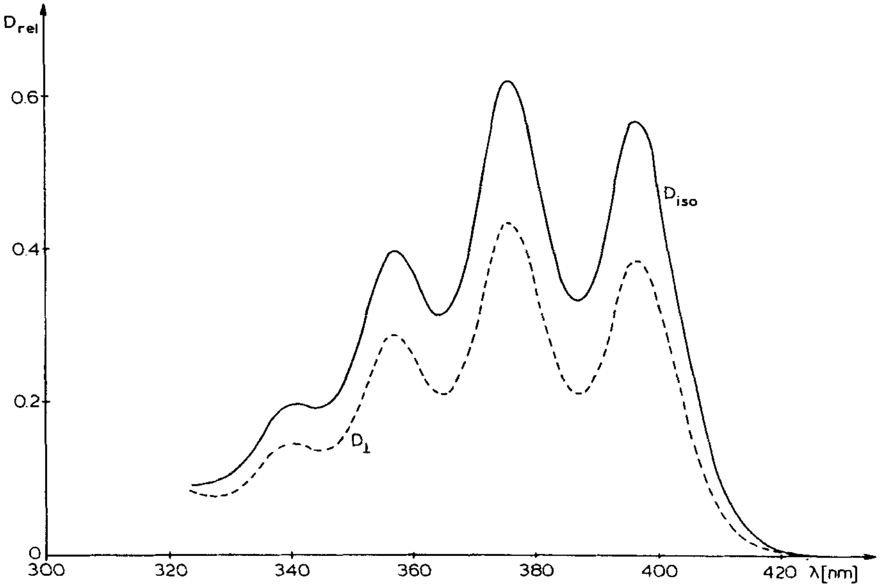


FIGURE 3d Spectra of 9.10-diphenylanthracene in ZLI 612.

an angle of about 45° between the optical axis and the molecule fixed z-axis is to be expected. The spectra (Figure 3b) imply that the Br–Br axis is slightly preferred.

Figure 3d shows the spectra of 9.10-diphenylanthracene in ZLI 612 as an example for a measurement without polarized light.

Bromo(2-diethylaminoethanolato)-Cu(II)[52] in solution[53] and in one of the crystalline modifications is dimeric[54,55,56] and therefore possesses an anisotropic molecular shape and can be oriented in a nematic solvent. The electronic spectrum in the wavelength range down to 325 nm consists of two bands, a relative intense ligand to metal charge transfer transition at 408 nm and a weak d-d-transition at c. 680 nm.

Figures 4a and b show the charge transfer band measured in N9 and ZLI 612. The dichroic ratios $R(R') > 1$ imply that the transition is polarized preferably parallel to the long molecular axis and from the symmetry, which is nearly C_{2h}, it can be concluded that the transition moment lies in the molecular plane.

The weak d-d-transition has been measured in N9 layers of 500 μm thickness. R is also greater than 1 but smaller than that of the charge-transfer-band. In the overlapping wavelength range, both measurements yield nearly the same value. From these facts it can be concluded that the

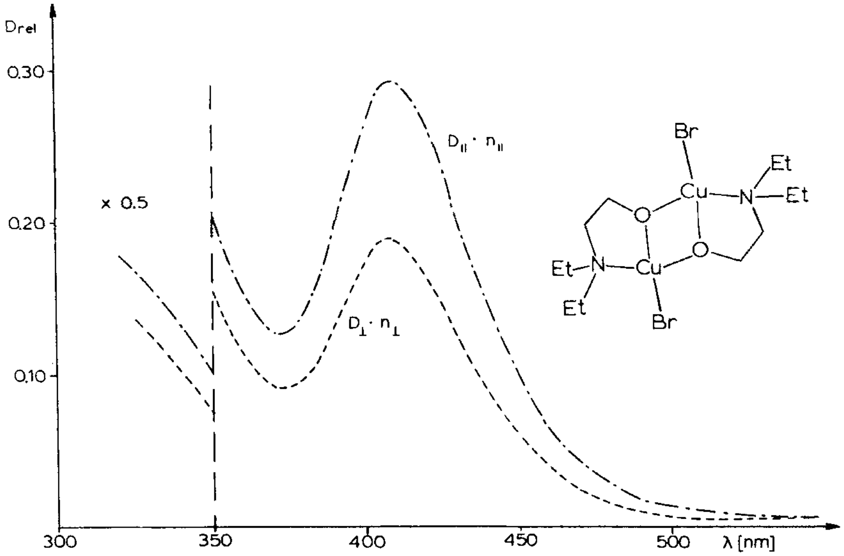


FIGURE 4a Charge-transfer-band of bromo(2-diethylaminoethanolato)-Cu(II) measured in N9.

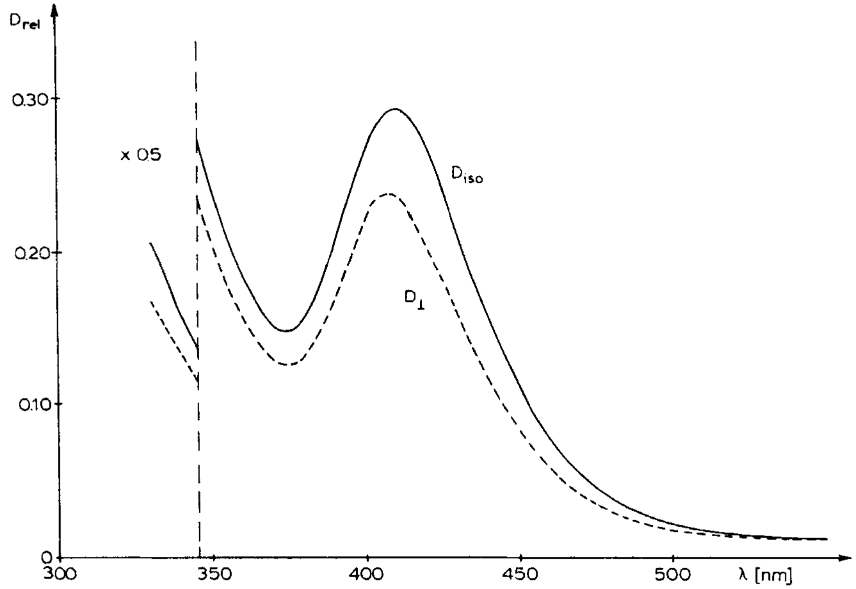


FIGURE 4b Charge-transfer-band of bromo(2-diethylaminoethanolato)-Cu(II) measured in ZLI 612.

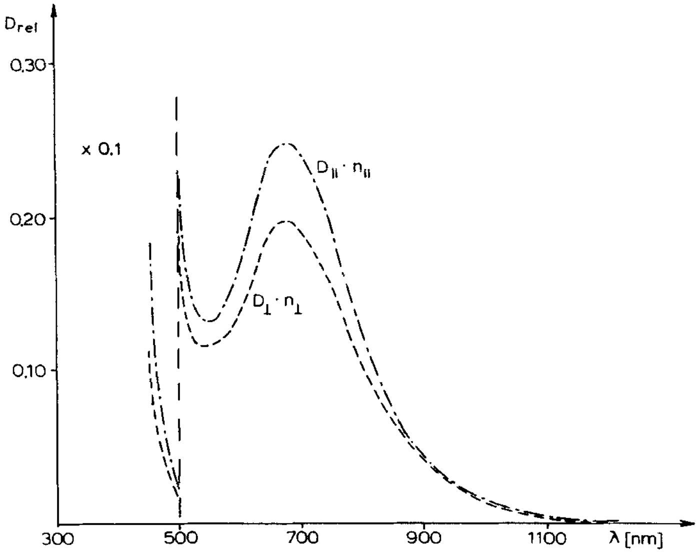


FIGURE 4c *d*-*d*-transition of bromo(2-diethylaminoethanolato)-Cu(II) measured in N9 with a cell of 500 μm thickness.

transition moment for the *d*-*d*-band also lies in the molecular plane but has a different direction from the transition moment for the 410 nm absorption. The measurements of the copper(II)-compound (in liquid crystals) together with further examples will be discussed in more detail in a forthcoming paper.[57]

5 CONCLUDING REMARKS

As shown by the present work linear dichroism measurements in nematic liquid crystals are an experimentally simple, rapid, and widely applicable method. It is possible to use nematic as well as compensated nematic phases. To get more exact order parameters the measured dichroic ratios have to be corrected for the contribution of the birefringence. The compensated nematic phases present the advantage of smaller birefringence, and of transparency down to about 240 nm. Nematic liquid crystals are transparent down to c. 300 nm and have a greater Δn, but they are easier to handle.

It is shown by the present work that the measurements can be done with natural as well as with polarized light. The homeotropic alignment (in order to measure without polarized light) can easily be achieved and no problems occur with the self polarization of the apparatus. Furthermore the difference between n_{iso} and $n_{\perp}$ is comparable to the birefringence of the compensated nematic phases. Therefore measurements without polarized light yield the greatest experimental simplification, but this method is restricted to substances which do not change between the two measuring temperatures.

With regard to the experimental effort and the range of applicability the spectroscopy in nematic liquid crystals and in stretched polymer sheets is comparable. By application of the reduction procedure to the measurement in nematic phases we could show that both methods give equivalent results. If polyethylene can be used the polymer sheet method has some advantage because of the transparency down to 210 nm.

For the measurement of weak transitions we think the liquid crystals to be suited better than the polymer sheets because in liquid crystals the experiment requires nearly the same technique as for thin films but makes more effort in foils. Examples investigated in thick layers are Bromo(2-diethylamino-ethanolato)-Cu(II) (vid. 4) and pyrene in order to get informations about the very weak bands.[33] Furthermore in nematic solvents it is possible to do measurements with and without polarized light, which is not possible in stretched sheets.

A drawback to all methods applying noncrystalline hosts is that without further information (e.g. the molecular symmetry) one gets only relative polarizations. Furthermore it is widely unknown if and to which extent the solute molecules are influenced by the interaction with the solvents.

Acknowledgements

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