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Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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Online publication date: 06 August 2010

To cite this Article Bauman, Danuta , Schulze, Hartmut and Kuball, Hans-Georg(2000) 'Linear dichroism of perylene derivatives in a nematic liquid crystal', Liquid Crystals, 27: 10, 1357 — 1367

To link to this Article: DOI: 10.1080/026782900423412

URL: http://dx.doi.org/10.1080/026782900423412

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LIQUID CRYSTALS, 2000, VOL. 27, NO. 10, 1357–1367

Linear dichroism of perylene derivatives in a nematic liquid crystal

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(*Received 12 January 2000; accepted 16 May 2000*)

The polarized absorption spectra of derivatives of 3,4,9-perylenetricarboxylic acid and of 3,4,9,10-perylenetetracarboxylic acid dissolved in the nematic liquid crystal mixture ZLI 1695 have been recorded as a function of temperature. On the basis of these spectra, the directions of the absorption transition moments with respect to the principle axes of the order tensor, and the order parameters S^* and D^* for perylene derivatives have been determined assuming a C_s or C_2 point symmetry group for the dyes molecules. From a generalized equation describing properties of anisotropic phases, the conditions necessary to determine a complete set of the order parameters and the pieces of possible information that can be obtained from the polarized optical spectroscopy are discussed.

1. Introduction

Dichroic dyes dissolved in nematic liquid crystals ('guest–host' systems) have been the subject of many investigations because of their applications both in science and technology. These systems can be used in optical spectroscopy for estimation of some molecular parameters of the dyes [1–5], as well as to obtain information about the long range orientational order of liquid crystals [6, 7] and about the molecular interactions between guest molecules and their liquid crystal environment [8, 9]. Guest–host liquid crystal display devices are also widely applicable because they display information in colour, with a wide viewing angle and high image brightness [10].

It was recently found [11] that some of derivatives of 3,4,9-perylenetricarboxylic acid and of 3,4,9,10-perylenetetracarboxylic acid can be used as dichroic dyes in guest–host liquid crystal displays. These dyes have a yellow to orange colour and emit fluorescent light in a spectral region advantageous for the human eye with a significantly high quantum yield. Moreover, they have good dichroic properties, are stable to the sunlight and do not significantly destabilize the mesophase of the nematic host.

In this paper we have studied in detail the absorption spectra of these dyes dissolved in the nematic liquid crystal mixture ZLI 1695 in the ultraviolet and visible spectral regions using polarized light in order to assign the electronic absorption bands, which have a very important meaning in optical spectroscopy. The derivatives of perylene have to be considered as dyes with molecular biaxiality. Therefore, they are characterized not only by the order parameter S, but also by the biaxial order parameter D. The aim of this paper is also the determination of these two order parameters as an evaluation of the polarization of the electronic absorption bands. S and D will be determined by a procedure developed earlier [2, 12] using standard equations. However, for molecules without symmetry, the method for determination of the order parameter has to be critically analysed because the orientation of the principal axis of the order tensor is not now determined by symmetry. The question as to the number of pieces of information obtained from the polarized spectroscopy for the determination of the order tensor has also to be answered in general.

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Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
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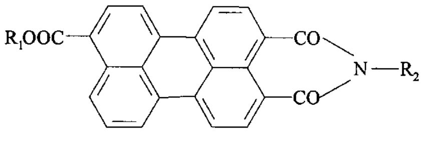
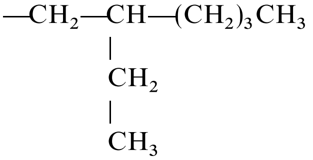
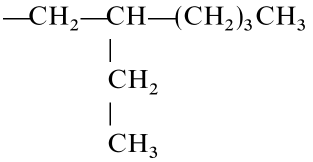
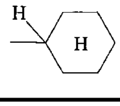
2. Materials and methods

The dyes investigated are described in the following sections.

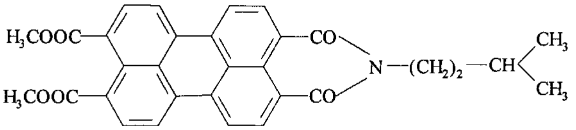
2.1. *Derivatives of 3,4,9-perylenetricarboxylic acid*



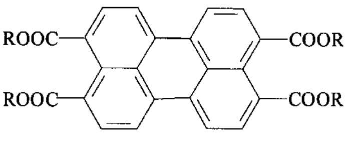
Dye code	R_1	R_2
1	 $-CH_2-\underset{\substack{\mid\\ CH_2\\ \mid\\ CH_3}}{CH}-(CH_2)_3CH_3$	$-CH_2CH_3$
2	 $-CH_2-\underset{\substack{\mid\\ CH_2\\ \mid\\ CH_3}}{CH}-(CH_2)_3CH_3$	$-CH_2CH_2OH$
3	$-(CH_2)_7CH_3$	$-(CH_2)_2CH(CH_3)_2$
4		$-(CH_2)_2CH(CH_3)_2$

2.2. *Derivatives of 3,4,9,10-perylenetetracarboxylic acid*

(a) Dye **5**



(b)



Dye code	R
6	$-(CH_2)_3CH_3$
7	$-(CH_2)_6CH_3$

The dyes were synthesized and chromatographically purified at the Institute of Dyes, Łódź University of Technology, Poland. They were added to the liquid crystal host in a concentration of 2×10^{-3} mol l^{-1}.

In order to measure the absorption spectra of the dyes in the UV spectral region we chose for our investigations the commercial liquid crystal ZLI 1695 (Merck, Darmstadt), which is a mixture of four 4-*n*-alkyl-4′-cyanobicyclohexanes and could be used down to about 210 nm. ZLI 1695 exhibits a nematic phase from about 13 to 72°C. The small concentration used for the dyes does not change the clearing point of the nematic host.

The polarized absorption spectra in the UV-Vis region were recorded using a Cary 17 spectrometer equipped with Glan polarizers. The measurements were carried out in 'sandwich' cells of 0.1 mm thickness. The temperature of the sample was regulated and controlled with an accuracy of ±0.2°. A planar homogeneous orientation of the liquid crystal and the dye molecules was achieved by applying an a.c. electric field $\mathbf{E} = 2 \times 10^6\ \mathrm{V\,m^{-1}}$ parallel to the plate surfaces of the cells. Further details concerning the experiment have been described elsewhere [4].

From the polarized absorption spectra the degree of anisotropy

$$R = \frac{\varepsilon_1 - \varepsilon_2}{3\varepsilon} \tag{1}$$

as a function of wavenumber has been obtained for all the dyes investigated in ZLI 1695. ε_1 and ε_2 are the molar decadic absorption coefficients for light polarized parallel and perpendicular to the optical axis of the liquid crystal sample, respectively. ε is the absorption coefficient determined by

$$\varepsilon = \frac{1}{3}(\varepsilon_1 + 2\varepsilon_2). \tag{2}$$

ε represents the molar decadic absorption coefficient which corresponds to the same temperature as that used for ε_1 and ε_2.

3. Theoretical background

3.1. *The method and its restriction*

The anisotropy of liquid crystalline phases arises because of the tendency of the mesogenic molecules to align along a certain preferred direction. The orientation of any molecule can be described using three Euler angles α, β, γ. The simplest complete description of the orientational order of an ensemble of molecules is the orientational distribution function $f(\alpha, \beta, \gamma)$, which gives the probability of finding a molecule at a particular orientation with respect to a space-fixed coordinate system. From this function one can define a set of orientational distribution coefficients g_{ijkl}, which represent the generalized form of the Saupe order tensor [13], where

$$g_{ijkl}=\frac{1}{4\pi}\int f(\alpha,\beta,\gamma)a_{ik}a_{jl}\sin\beta\,\mathrm{d}\alpha\,\mathrm{d}\beta\,\mathrm{d}\gamma. \qquad (3)$$

$a_{ij}(\alpha,\beta,\gamma)$ are the elements of an orthogonal transformation matrix from the space-fixed (x_i') to the molecule-fixed (x_i) Cartesian coordinate system. The molecular decadic absorption coefficients of a uniaxial sample, ε_1 and ε_2 are given by [14]

$$\varepsilon_1=\sum_{ij}g_{ij33}\varepsilon_{ij}=\sum_{ij}a_{ij}^2g^*_{jj33}\varepsilon^+_{ii} \qquad (4)$$

$$\varepsilon_2=\sum_{ij}g_{ij11}\varepsilon_{ij}=\sum_{ij}a_{ij}^2g^*_{jj11}\varepsilon^+_{ii} \qquad (5)$$

with

$$g^*_{ii11}=g^*_{ii22}$$

and

$$\varepsilon=\frac{1}{3}\sum_i\varepsilon^+_{ii}. \qquad (6)$$

ε^+_{ii} are the elements of the absorption tensor for light beams polarized linearly parallel to the x_i^+ axes in a completely oriented system. The x_i^+ axes are the principal axes of the absorption tensor ε_{ij} [2, 3, 14, 15]. a_{ij} are now the elements of the orthogonal matrix which transform the x_i^* coordinates into the x_i^+ coordinates. The x_i^* coordinates refer to the principal axes of the order tensor g_{ijkk} ($k=1,2,3$). The following convention for numbering the axes is used: $g^*_{3333}\geqslant g^*_{2233}\geqslant g^*_{1133}$ [3] with x_3^* as the 'orientation axis'. For molecules with a point symmetry group different from C_1, C_i, C_2, C_s and C_{2h} there is no temperature dependence of the orientation of the x_i^* axes relative to the molecular frame. Then the linear dichroism $\varepsilon_1-\varepsilon_2$ can be described by [14]

$$\varepsilon_1-\varepsilon_2=\frac{3}{2}(\varepsilon^*_{33}-\varepsilon)S^*+\frac{\sqrt{3}}{2}(\varepsilon^*_{22}-\varepsilon^*_{11})D^* \qquad (7)$$

because in this case the ε^*_{ii} are temperature independent. S^* and D^* are Saupe's order parameters [13], which are sufficient to characterize the long range orientational order of a uniaxial phase with respect to the absorption processes if the phase is characterized by a molecular biaxial orientational distribution. They are defined by

$$S^*=\frac{1}{2}(3g^*_{3333}-1) \qquad (8)$$

$$D^*=\frac{\sqrt{3}}{2}(2g^*_{2233}+g^*_{3333}-1)=\frac{\sqrt{3}}{2}(g^*_{2233}-g^*_{1133}). \qquad (9)$$

S^* characterizes the orientational order of the x_3^* axis with respect to the optical axis of the uniaxial phase and is dependent only on the angle β, whereas D^* is a measure of the deviation from a rotationally symmetric distribution of the molecules about their x_3^* axis and depends on the angles β and γ. The relation between the order parameters S^* and D^* and the degree of anisotropy R is [14]

$$R=\frac{1}{2}(3q^*_{33}-1)S^*+\frac{\sqrt{3}}{2}(q^*_{22}-q^*_{11})D^* \qquad (10)$$

where

$$q^*_{ii}=\frac{\varepsilon^*_{ii}}{3\varepsilon};\qquad 0\leqslant q^*_{ii}\leqslant 1;\qquad \sum_i q^*_{ii}=1.$$

If in the absorption spectrum there exist two pure polarized bands at $\bar{\nu}_1$ and $\bar{\nu}_2$ for which the direction of the related transition moments with respect to the molecular axes are different, and the principal axes are determined by symmetry, then the order parameters S^* and D^* can be directly determined from the experimental data for $R(\bar{\nu}_1)$ and $R(\bar{\nu}_2)$. In this case

$$S^*=R(\bar{\nu}_1) \qquad (11)$$

and

$$D^*=\frac{1}{\sqrt{3}}[2R(\bar{\nu}_2)+R(\bar{\nu}_1)]. \qquad (12)$$

For molecules with only one purely polarized absorption band and other bands of mixed polarization, i.e. overlapping bands, the following procedure must be used in order to determine the $q^*_{ii}(\bar{\nu})$ and S^* and D^* values. For the temperature dependent degree of anisotropy of two different polarized transitions at the wavenumbers $\bar{\nu}_1$ and $\bar{\nu}_2$ one can obtain

$$R(\bar{\nu}_1,T)=\frac{1}{2}[3q^*_{33}(\bar{\nu}_1)-1]S^*(T)+\frac{\sqrt{3}}{2}[q^*_{22}(\bar{\nu}_1)-q^*_{11}(\bar{\nu}_1)]D^*(T) \qquad (13)$$

$$R(\bar{\nu}_2,T)=\frac{1}{2}[3q^*_{33}(\bar{\nu}_2)-1]S^*(T)+\frac{\sqrt{3}}{2}[q^*_{22}(\bar{\nu}_2)-q^*_{11}(\bar{\nu}_2)]D^*(T). \qquad (14)$$

Because $R(\bar{\nu}_1,T)$ as well as $R(\bar{\nu}_2,T)$ are dependent on S^* and D^*, the following relation is valid [2, 3]

$$R(\bar{\nu}_2,T)=\Phi[R(\bar{\nu}_1,T)] \qquad (15)$$

taking $D^*=f(S^*,\delta)$ as given in [16] and assuming the parameter δ to be independent of temperature. If the band at given $\bar{\nu}_\beta$ is purely polarized, then $q^*_{ii}(\bar{\nu}_\beta)$ is equal to zero or one for $i=1$, 2, or 3, depending on the polarization direction. Then using a fitting procedure with the variation of all parameters $q^*_{ii}(\bar{\nu}_2)$, as well as the δ value within their limits, the relation given by equation (15) can be calculated. The sum of the squares of the distances of the experimental points from the calculated curves vertical to the tangent is evaluated and taken as a measure of the quality of approximation by the chosen parameter set.

For perylene, which is the main skeleton of the molecular structure of the dyes investigated, a point symmetry group D_{2h} is assumed. Thulstrup *et al.* [1] had assigned the absorption spectrum of perylene assuming the existence of two purely polarized bands due to π-π* transitions. The substituents in the perylene ring systems in derivatives **1** to **7** cause a lowering of the symmetry and simultaneously a shift of the absorption bands, leading to an increased overlapping of the different bands. Therefore, in the substituted perylenes only one purely polarized band seems to be preserved. The degree of anisotropy of the long wavelength band of **1** to **7** is independent of the wavelength. This is a strong hint that this band is purely polarized. However, for this band none of the $q^*_{ii}(\bar{\nu})$, $i = 1, 2, 3$, have to be equal to 1, because the direction of the electric dipole transition moments may not coincide with the principal axis of the order tensor in the case of the substituted perylene derivatives. Because of the low symmetry of the molecules of **1** to **7**, the above-described method cannot be applied to the determination of the order parameters and the elements of the order tensor without additional approximation or information. Previously, we had used this procedure in order to assign the absorption spectrum of β,β′-dimethylmesobilirubin XIIIα [12] (C_2 point symmetry group), because we had been able to use additional relations derived from exciton theory. Now, for the perylene derivatives we attempt to answer the question about how many pieces of information can be obtained from various absorption bands with mixed polarization when only one axis of the principal axes of the order tensor is fixed by symmetry.

3.2. *The available information—generalization of the method*

The orientational distribution coefficients g_{ijkl} connect molecular properties X_{ij} with the corresponding measurable properties of an anisotropic sample which are described by a second-rank tensor Y_{kl} [17]

$$Y_{kl} = \sum_i \sum_j g_{ijkl} X_{ij} \tag{16}$$

as is given in a special form in equation (4). For an absorption process (IR, Vis, UV) the molecular property $X^{(s)}_{ij}$ of the sth absorption band is given by [18]

$$X^{(s)}_{ij} = \varepsilon^{NnKk}_{ij}(\bar{\nu}) = \frac{B\bar{\nu}}{4} \sum_n \sum_{Kk} D^{NnKk}_{ij} F^{NnKk}(\bar{\nu}) \tag{17}$$

where $D^{NnKk}_{ij} = \langle \mu_i \rangle_{NnKk} \langle \mu_j \rangle_{NnKk}$ is the electric dipole transition moment tensor and $F^{NnKk}(\bar{\nu})$ is the band shape for the transition s ($|Nn\rangle \rightarrow |Kk\rangle$). The ε_{ij} are the elements of the symmetric absorption tensor. In this case Y_{kl} is also symmetric, because of the relation

$$g_{ijkl} = g_{jilk}. \tag{18}$$

The symmetry of the liquid crystalline phase reduces the number of measurable independent quantities Y_{kl} as shown in table 1. This table presents the number of independent pieces of information (Y_{kl}) for various phase symmetries and the number of coordinates of the orientational distribution coefficients (g_{ijkl}) which are necessary for a complete description of order if the phase consists of molecules with the point symmetry group C_1 and D_2, respectively. It is seen that for biaxial molecules without any symmetry (C_1), five independent g_{ijkl} have still to be determined from the only available quantity $Y_{33} = \varepsilon_1$ and the $\mathrm{Tr}\{Y_{kk}\} = 3\varepsilon$, i.e. from the absorption measurements using linearly polarized light only one independent measureable quantity ε_1 can be obtained for an anisotropic sample. The absorption coefficient of an isotropic phase ε has to be measured additionally. Because ε_1 and ε cannot be measured at the same temperature for liquid crystalline phases, ε_1 and ε_2 are measured instead, and then ε can be calculated by equation (2). The additional pieces of information needed are the absorption tensor $\varepsilon_{ij}(\bar{\nu}_q)$ for different positions $\bar{\nu}_q$ in the spectrum. For these different wavenumbers $\bar{\nu}_q$, the $\varepsilon_1(\bar{\nu}_q)$ have to be measured; here the wavenumbers $\bar{\nu}_q$ have to selected with respect to characteristic points of the absorption spectrum. For a molecule of point symmetry group C_1 and C_i, there are five, for C_2, C_s and C_{2h}, there are three, and for all other symmetries, there are two measurements at different wavenumbers necessary [19], so requiring five, three or two purely polarized transitions available in the UV, Vis or IR spectra.

Let us now generalize the method allowing the complete description of the orientational order necessary to describe effects of second rank tensors like the absorption process. On the basis of equations (4) and (5) and taking into account that $g_{ij11} + g_{ij22} = 2g_{ij11} = \delta_{ij} - g_{ij33}$, we obtain the following relation for the linear dichroism:

$$\varepsilon_1 - \varepsilon_2 = 1/2 \sum_{ij} (3g_{ij33} - \delta_{ij})\varepsilon_{ij}. \tag{19}$$

Then, from equation (1) follows:

$$1/3(2R + 1) = \sum_{ij} g_{ij33} q_{ij} \tag{20}$$

Table 1. Independently measurable quantities Y_{kl} and number of independent orientational distribution coefficients g_{ijkl} for phases and molecules of different point symmetry groups.

Point symmetry group of the phase (local symmetry)		Symmetry of the phase	Example of the phase	Independent ${}^{s}Y^{(\beta)\,a}_{kl}$	Number of g_{ijkl} for two point symmetry groups of the molecule	
Chiral	Achiral				C_1	D_2
C_1		(biaxial)		${}^{s}Y^{(\beta)}_{22}$, ${}^{s}Y^{(\beta)}_{33}$ ${}^{s}Y^{(\beta)}_{12} = {}^{s}Y^{(\beta)}_{21}$, ${}^{s}Y^{(\beta)}_{13} = {}^{s}Y^{(\beta)}_{31}$, ${}^{s}Y^{(\beta)}_{23} = {}^{s}Y^{(\beta)}_{32}$	25	10
(C_2)		biaxial	smectic C*	${}^{s}Y^{(\beta)}_{22}$, ${}^{s}Y^{(\beta)}_{33}$ ${}^{s}Y^{(\beta)}_{13}$	15	6
	C_{2h}	biaxial	smectic C	${}^{s}Y^{(\beta)}_{22}$, ${}^{s}Y^{(\beta)}_{33}$, ${}^{s}Y^{(\beta)}_{13}$	15	6
(D_2)		biaxial	chiral nematic N* smectic C*	${}^{s}Y^{(\beta)}_{22}$, ${}^{s}Y^{(\beta)}_{33}$	10	4
D_∞		uniaxial	chiral nematic N* smectic C*	${}^{s}Y^{(\beta)}_{33}$	5	2
	$D_{\infty h}$	uniaxial	nematic smectic A	${}^{s}Y^{(\beta)}_{33}$	5	2

[a] Superscript s means the symmetric tensor; superscript (β) means the transition $|Nn\rangle \rightarrow |Kk\rangle$.

and

$$R = \sum_{ij} S_{ij} q_{ij} \tag{21}$$

where

$$q_{ij} = \frac{\varepsilon_{ij}}{\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33}}$$

and S_{ij} are the coordinates of the Saupe order tensor [13] of the guest molecule. Introducing the unit vector parallel to the given transition moment direction b_i

$$b_i = \frac{\langle \mu_i \rangle_{NnKk}}{(\langle \mu_1 \rangle^2_{NnKk} + \langle \mu_2 \rangle^2_{NnKk} + \langle \mu_3 \rangle^2_{NnKk})^{1/2}} \tag{22}$$

it follows that

$$\frac{1}{3}[2R^{(s)}(\bar{\nu}_q, T) + 1] = \tilde{\underline{b}}^{(s)} \underline{\underline{g}}(T) \underline{b}^{(s)}. \tag{23}$$

Instead of equation (23), the following equation can also be used:

$$R^{(s)}(\bar{\nu}_q, T) = \tilde{\underline{b}}^{(s)} \underline{\underline{S}}(T) \underline{b}^{(s)} \tag{24}$$

where $\bar{\nu}_q$ is the qth wavenumber in the sth absorption band with polarization direction $\underline{b}^{(s)}$. If in the spectrum there exist five purely polarized bands $\underline{b}^{(s)}$ ($s = 1, \ldots, 5$), with equations (23) or (24) five linear equations with respect to the coordinates of the elements of the order tensor can be written

$$\begin{aligned} Q^{(s)}(\bar{\nu}_q, T) &= \frac{1}{3}[2R^{(s)}(\bar{\nu}_q, T) + 1] - b_3^{(s)2} \\ &= (b_1^{(s)2} - b_3^{(s)2}) g_{1133} + (b_2^{(s)2} - b_3^{(s)2}) g_{2233} \\ &\quad + 2b_1^{(s)} b_2^{(s)} g_{1233} + 2b_1^{(s)} b_3^{(s)} g_{1333} + 2b_2^{(s)} b_3^{(s)} g_{2333} \end{aligned} \tag{25}$$

with which all independent coordinates g_{ij33} can be obtained [15] from the degree of anisotropy $R^{(s)}(\bar{\nu}_q, T)$ of the absorption spectrum measured within the sth band at the wavenumbers $\bar{\nu}_q$ ($q = 1, \ldots, 5$) of the pure bands $s = 1, \ldots, 5$. With the column vector $\underline{Q} = \{Q^{(1)}, \ldots, Q^{(5)}\}$ of the five $Q^{(s)}(\bar{\nu}_q, T)$ with $s = q = 1, 2, \ldots, 5$ and the five coordinates of the order tensor written as a column vector $\underline{g} = \{g_{1133}, g_{2233}, g_{1233}, g_{1333}, g_{2333}\}$ and the matrix of the coefficients given by the $b_i b_j$ terms $\underline{\underline{B}}$ in equation (5), the linear set of the equation can be given by

$$\underline{\underline{B}}\underline{g} = \underline{Q}. \tag{26}$$

With the help of the Kramer rules, the coordinates of the order tensor g_{ij33} for the given temperature T can be calculated if the set of inhomogeneous linear equation (25) has a solution. It should be noted, however, that even in the case of purely polarized bands, certain situations must be excluded that follow from equation (25). No more than three absorption transition moments may lie in the same plane or, more generally, possess a common normal, i.e. only then are all five transition moment directions independent. Moreover, only then is the rank of the matrix of the coefficients of the system of linear equations given as 5 by the $\underline{\underline{B}}$ of the b_i. This is analogous to ^{2}H NMR spectroscopy where the same condition holds for three independent C–D bond directions [14*a*, 15].

In the UV-Vis spectrum, five independent transition moments are usually not observed, but they can often be found in IR spectra. In the absorption spectrum measured in the UV-Vis region, mostly overlapping bands occur and the question arises whether from the overlap ratio, if known, any additional information can be derived. Let us define the overlap ratio as follows

$$r^{(s)}(\bar{\nu}_q) = \frac{\varepsilon^{(s)}(\bar{\nu}_q)}{\varepsilon(\bar{\nu}_q)} \tag{27}$$

where $\varepsilon^{(s)}(\bar{\nu}_q)$ is the absorption coefficient at the wavenumber $\bar{\nu}_q$ for a given transition s. $\Sigma\, \varepsilon^{(s)}(\bar{\nu}_q) = \varepsilon(\bar{\nu}_q)$ at a given wavenumber $\bar{\nu}_q$ and $\Sigma_s\, r^{(s)}(\bar{\nu}_q) = 1$ is the sum over all the transition s contributing to the band at the wavenumber $\bar{\nu}_q$. By analogy with equations (23) and (24), the following relation can be obtained

$$\frac{1}{3}[2R^{(s)}(\bar{\nu}_q, T) + 1] = \sum_s r^{(s)}(\bar{\nu}_q)\underline{b}^{(s)}\underline{\underline{g}}(T)\underline{b}^{(s)} \tag{28}$$

or

$$R^{(s)}(\bar{\nu}_q, T) = \sum_s r^{(s)}(\bar{\nu}_q)\underline{b}^{(s)}\underline{\underline{S}}(T)\underline{b}^{(s)}. \tag{29}$$

Using equation (29) instead of (24) for the matrix of the coefficients $\underline{\underline{B}}$ of (25), then a sum of coefficient matrices with the weighting factor $r^{(s)}(\bar{\nu}_q)$ is obtained. If there are less than five independent transition moments, the rank of the matrices is smaller than five. Thus, the coordinates of the order tensor cannot be determined completely. This means that overlapping of bands—even with a known $r^{(s)}(\bar{\nu}_q)$—does not increase the number of independent pieces of information.

The question has to be raised as to how it is possible to ascertain how many pieces of independent information are available from a measured UV spectrum. This cannot be determined by an analysis of the frequency dependence of the degree of anisotropy of the absorption spectra, because this dependence can also be a consequence of band overlapping—which does not lead to new information which can be utilized for the calculation. To answer the question whether a spectrum can yield sufficient information, a quantum theoretical calculation of the transitions in the accessible spectral region with independent transition moment directions is another possible approach. But at present this is not always possible with sufficient accuracy. A direct analysis of the absorption coefficient $\varepsilon_1(\bar{\nu}_i, T_j)$ or $\varepsilon_2(\bar{\nu}_i, T_j)$ with respect to $Q^{(s)}(\bar{\nu}_q, T_j)$ or $R^{(s)}(\bar{\nu}_q, T_j)$ for different wavenumbers and for different temperatures may offer a new possibility. To examine this, the absorption values at n different wavenumbers and m different temperatures have to be measured. From equation (26) with $n = m$ different temperatures and wavenumbers the following matrix equation can be obtained

$$\underline{\underline{B}}\begin{pmatrix} g_{1133}(T_1) & \dots & g_{1133}(T_n) \\ \vdots & & \\ g_{2233}(T_1) & \dots & g_{2333}(T_n) \end{pmatrix} = \underline{\underline{B}}\,\underline{\underline{G}} = \begin{pmatrix} Q^{(1)}(T_1) & \dots & Q^{(1)}(T_n) \\ \vdots & & \\ Q^{(5)}(T_1) & \dots & Q^{(5)}(T_n) \end{pmatrix} = \underline{\underline{Q}}. \tag{30}$$

The rank of $\underline{\underline{B}}\,\underline{\underline{G}}$ determines the rank of $\underline{\underline{Q}}$. Because from the symmetry of the molecules the number of independent tensor coordinates of the order tensors for different temperatures $\underline{\underline{G}}$ is known, the rank of the experimentally determined matrix $\underline{\underline{Q}}$ then leads to the number of independent pieces of information which can be used to determine the $g_{ij33}(T)$. Thus the determination of the rank of $\underline{\underline{Q}}$ allows us to answer the question concerning how many pieces of information are in a set of such measurements and thus to answer the question whether the complete order tensor can or cannot be determined from the accessible absorption spectra. The rank of $\underline{\underline{Q}}$ is given by the rank of $\underline{\underline{B}}$ if $\underline{\underline{G}}$ is a regular matrix, which may not often be the case because of the kind of temperature function of the tensor coordinates $g_{ij33}(T)$. Moreover, the experimental errors in the degree of anisotropy can restrict this type of analysis by a bad ‘conditioning of the matrix $\underline{\underline{Q}}$’.

Is there, we may ask, a possibility of using the temperature dependence of g_{ij33} as an additional source of information to substitute for information from the bond direction? To answer the question, equation (30) can be written as

$$\widetilde{\underline{\underline{B}}\,\underline{\underline{G}}} = \tilde{\underline{\underline{G}}}\tilde{\underline{\underline{B}}} = \tilde{\underline{\underline{Q}}} \tag{31}$$

and

$$\tilde{\underline{\underline{G}}}\tilde{\underline{\underline{B}}} = \tilde{\underline{\underline{Q}}} \tag{32}$$

where equation (32) can be used to determine the bond direction from a known $\underline{\underline{G}}$ and $\underline{\underline{Q}}$. To answer the question about the number of pieces of information from which the rank of the $\underline{\underline{G}}$ matrix has to be determined, this may be five, in general. Then five independent directions could be measured. This is not however true, as we have seen before in the $R(\bar{\nu}_1)$, $R(\bar{\nu}_2)$ procedure

[2, 3] from which it can be seen that from experience the rank is usually only three. A further systematic analysis seems necessary to extend these analyses.

4. Results

Figures 1 and 2 show as examples the polarized absorption spectra, ε_1 and ε_2 and the degree of anisotropy, R as a function of wavenumber at a temperature $T = 38°C$ for dyes **4** and **7** in ZLI-1695. The structure of the dyes **1** to **7** (see §2) suggests that they have at best C_s symmetry, but C_2 symmetry cannot be excluded. For the case of C_s or C_2 symmetry of the compounds, three directions of the transition moments should be known to obtain the whole order tensor. From the discussion in the previous section it follows that only two independent pieces of information are available from the measurement of the spectra at different wavenumbers $\bar{\nu}_q$ (figures 1 and 2). In order to use the temperature dependence as a source of additional information for the evaluation of the order parameters, the Luckhurst relation $D^* = f(S^*, \delta)$ [16] has to be used. This means that for the determination of the order parameters S^* and D^*, as well as the diagonal elements of the absorption tensor with respect to the principal axes of the order tensor, the degree of anisotropy of at least two variously polarized transitions at different wavenumbers $\bar{\nu}_1$ and $\bar{\nu}_2$ should be chosen. As $\bar{\nu}_1$ for all the dyes investigated, the maximum position for the long wavelength absorption band was taken, because R has here a maximal value and is almost frequency independent over the band. Therefore, one can assume to a good approximation that this band is purely polarized. There are no further purely polarized bands in the accessible spectral region and thus $\bar{\nu}_2$ was chosen as the wavenumber at which R is minimal. Table 2 gathers together the values of $R(\bar{\nu}_1)$ and $R(\bar{\nu}_2)$ at three temperatures. Now, the transition moment directions should be assigned with respect to the x_i^* axes; this means the relative absorption coefficients $q_{ii}^*(\bar{\nu})$ for the bands at $\bar{\nu}_1$ and $\bar{\nu}_2$. In general, there are 6 unknown q_{ii}^* parameters ($i = 1, 2, 3$ for $\bar{\nu}_1$ and $\bar{\nu}_2$). The number of these parameters can, however, be reduced in the case of molecular symmetry, as was shown earlier [2–4, 12]. Moreover, three criteria should be taken into account: (1) the positions of the experimental values of the degree of anisotropy in the $R(\bar{\nu}_1)$, $R(\bar{\nu}_2)$ plane; (2) the slope of the curve $R(\bar{\nu}_1, T) = \Phi[R(\bar{\nu}_2, T)]$; and (3) its curvature [3]. In order to do this, one has to assume that the molecules are of a symmetry different from C_1, C_i, C_2, C_s, and C_{2h}, because the decomposition

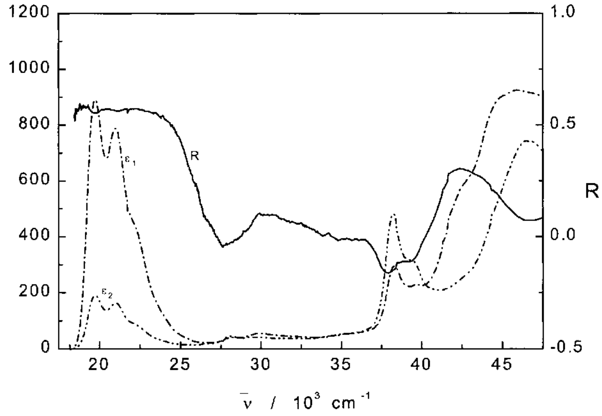


Figure 1. Polarized absorption spectra ε_1 and ε_2, and degree of anisotropy R, for dye **4** in ZLI 1695 at $T = 38°C$.

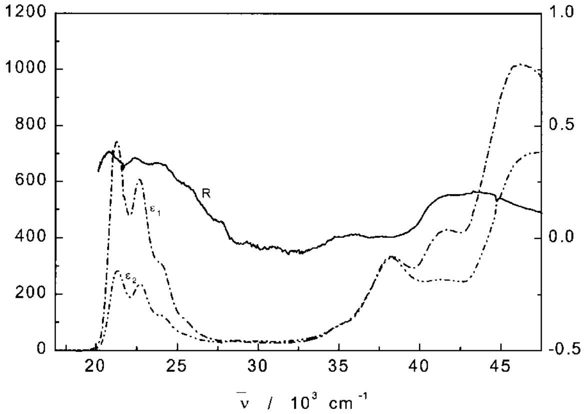


Figure 2. Polarized absorption spectra ε_1 and ε_2, and degree of anisotropy R, for dye **7** in ZLI 1695 at $T = 38°C$.

Table 2. Highest $R(\bar{\nu}_1)$ and lowest $R(\bar{\nu}_2)$ values of the degree of anisotropy for dyes **1** to **7** in ZLI 1695.

			$T = 28°C$		$T = 48°C$		$T = 68°C$	
Dye code	$\bar{\nu}_1/10^3\,cm^{-1}$	$\bar{\nu}_2/10^3\,cm^{-1}$	$R(\bar{\nu}_1)$	$R(\bar{\nu}_2)$	$R(\bar{\nu}_1)$	$R(\bar{\nu}_2)$	$R(\bar{\nu}_1)$	$R(\bar{\nu}_2)$
1	19.80	38.31	0.455	− 0.076	0.438	− 0.059	0.349	− 0.053
2	19.80	38.31	0.488	− 0.080	0.460	− 0.065	0.331	− 0.041
3	19.80	38.24	0.517	− 0.111	0.504	− 0.110	0.317	− 0.067
4	19.76	38.24	0.548	− 0.123	0.545	− 0.128	0.362	− 0.088
5	19.92	38.17	0.607	− 0.174	0.568	− 0.131	0.415	− 0.111
6	21.32	38.31	0.318	0.023	0.303	0.039	0.209	0.032
7	21.32	38.31	0.361	0.014	0.342	0.031	0.214	0.040

of the order triangle given in [3] has been developed only for molecules with symmetry-fixed principal axes of the order tensor.

To a first approximation, to evaluate the data obtained for the dyes investigated, C_s symmetry has been assumed. In such a case, symmetry dictates that the observed electronic transitions lie in the plane of the aromatic skeleton. In the same plane lies the orientation axis x^*_3 which is approximately correlated with the molecular long axis. Using additional criteria (1) to (3), we have concluded that the transition moments related to the absorption bands at $\bar{\nu}_1$ and $\bar{\nu}_2$ lie in the x^*_2, x^*_3 plane, and thus $q^*_{11} = 0$. Now, using computer simulation, the parameters q^*_{22} and q^*_{33} for the bands at $\bar{\nu}_1$ and $\bar{\nu}_2$ could be determined. However, by means of a simulation program, many possible solutions have been obtained within the experimental error, probably connected with the fact that the procedure used had been developed for molecules with higher symmetry. Therefore, additional information was necessary in order to choose the proper solution. For this purpose the values of the degree of anisotropy for other wavenumber regions such as $R(\bar{\nu}_2)$ have been considered and q^*_{22} and q^*_{33} parameters obtained for the band at $\bar{\nu}_1$ have been compared. It has always been assumed that the transition moments corresponding to the band at each $\bar{\nu}_2$ lie in the x^*_2, x^*_3 plane. Nevertheless, by utilizing such a procedure, no consistent results for dyes **6** and **7** have been obtained. It seems that the alkyl chains cause the molecular symmetry of these dyes to be lower than C_s. Taking into account the steric interactions between the two alkyl chains attached at one side of the perylene skeleton, it is possible to suppose that one chain comes out in front of and the second comes out behind the x^*_2, x^*_3 plane. In this case, the point symmetry group C_2 can be considered, meaning that there exists one transition polarized parallel to the C_2 rotation axis, whereas others lie in a plane perpendicular to it. Therefore, it has been assumed that $q^*_{11} = q^*_{22} = 0$ and $q^*_{33} = 1$ for the band at $\bar{\nu}_1$ and that all other bands have q^*_{ii} parameters different from zero. The values of q^*_{ii} for all bands distinguished in the absorption spectra of dyes **1** to **5** are gathered in table 3, and those of dyes **6** and **7** are shown in table 4. The q^*_{ii} parameters presented in tables 3 and 4 have been chosen from among many possible solutions in such a way that, by taking various wavenumbers as $\bar{\nu}_2$, the same values of q^*_{ii} for the band at $\bar{\nu}_1$ have always been obtained.

Knowing the relative absorption coefficients q^*_{ii}, the order parameters S^* and D^* can be calculated from equation (10). The values of S^* and D^* for all the dyes investigated using ZLI 1695 at various temperatures are gathered together in table 5. It is necessary to mention here that both order parameters have been determined taking various bands as the $\bar{\nu}_2$ region. It has been ascertained that the S^* values obtained for various $\bar{\nu}_2$ differ only slightly; they are in fact almost identical within experimental uncertainty. However, the D^* values depend on the chosen $\bar{\nu}_2$ region. Therefore, in table 5, two D^* values for every dye are listed: the first D^* values have been calculated for $\bar{\nu}_2$ corresponding to $R_{\min}$ (given in table 1), whereas the second $\bar{D}^*$ is the average value.

Knowledge of the q^*_{ii} parameters also gives the possibility of obtaining reduced absorption spectra, i.e. the spectra decomposed into the tensor coordinates with respect to the x^*_i ($i = 1, 2, 3$) axes [1–4]. Figures 3 and 4 show the reduced spectra for dyes **3** and **4** and for dyes **5** and **7** as examples. Solid curves in these figures represent the total sum of light absorption due to all the transition moment coordinates directed along orientation axis x^*_3 (ε^*_{33}), while for the dashed curves, we are concerned with all the transition moment components directed along the x^*_2 axis (ε^*_{22}). Additionally, in figure 4 (*b*) a dotted curve is presented; this is related to the absorption due to all the transition moment components directed

Table 3. Values of $q^*_{22}(\bar{\nu}_1)$ for different absorption bands of dyes **1** to **5** in ZLI 1695. $q^*_{11}(\bar{\nu}_1) = 0$; $q^*_{11}(\bar{\nu}_2) = 0$.

Dye code	$\bar{\nu}_1/10^3\,\mathrm{cm}^{-1}$	q^*_{22}	$\bar{\nu}_2/10^3\,\mathrm{cm}^{-1}$	q^*_{22}	$\bar{\nu}_2/10^3\,\mathrm{cm}^{-1}$	q^*_{22}	$\bar{\nu}_2/10^3\,\mathrm{cm}^{-1}$	q^*_{22}
1	19.80	0.02	38.31	0.81	42.37	0.26	46.73	0.66
2	19.80	0.02	38.31	0.86	42.37	0.40	46.95	0.65
3	19.80	0.12	38.24	0.80	42.37	0.39	46.51	0.64
4	19.76	0.01	38.24	0.88	42.37	0.34	46.73	0.62
5	19.92	0.02	38.17	0.88	42.55	0.31	47.17	0.50

Table 4. Values of $q^*_{ii}(\bar{\nu}_2)$ for different absorption bands of dyes **6** and **7** in ZLI 1695. $q^*_{33}(\bar{\nu}_1) = 1$.

Dye code	$\bar{\nu}_2/10^3\,\mathrm{cm}^{-1}$	q^*_{22}	q^*_{33}	$\bar{\nu}_2/10^3\,\mathrm{cm}^{-1}$	q^*_{22}	q^*_{33}	$\bar{\nu}_2/10^3\,\mathrm{cm}^{-1}$	q^*_{22}	q^*_{33}
6	38.31	0.52	0.26	42.55	0.34	060	47.62	0.60	0.29
7	38.31	0.67	0.15	42.55	0.39	0.57	47.62	0.54	0.36

Table 5. Order parameters S^* and D^* versus temperature for dyes **1** to **7** in ZLI 1695 ($\Delta S^* = \pm 0.01$, $\Delta D^* = \pm 0.02$).

T/°C	Dye code	S^*	D^{*a}	$\bar{D}^*$	Dye code	S^*	D^{*a}	$\bar{D}^*$
28	**1**	0.47	0.04	0.08	**5**	0.63	0.03	0.07
38		0.47	0.04	0.07		0.61	0.01	0.05
48		0.45	0.05	0.10		0.58	0.07	0.15
58		0.40	0.03	0.09		0.51	0.03	0.12
65		0.37	0.03	0.08		0.46	0.02	0.06
68		0.36	0.03	0.06		0.43	0.03	0.13
70		0.33	0.05	0.13		0.38	0.03	0.11
28	**2**	0.50	0.09	0.12	**6**	0.32	0.22	0.23
38		0.50	0.07	0.15		0.31	0.23	0.26
48		0.47	0.10	0.20		0.30	0.28	0.29
58		0.43	0.08	0.21		0.26	0.23	0.26
65		0.36	0.06	0.17		0.23	0.21	0.23
68		0.34	0.08	0.17		0.21	0.21	0.22
70		0.31	0.10	0.20		0.17	0.17	0.19
28	**3**	0.64	0.02	0.04	**7**	0.36	0.27	0.27
38		0.63	0.01	0.07		0.35	0.24	0.24
48		0.61	0.01	0.10		0.34	0.29	0.30
58		0.53	0.02	0.12		0.30	0.27	0.28
65		0.46	0.02	0.10		0.27	0.26	0.27
68		0.38	0.01	0.08		0.21	0.23	0.23
70		0.29	0.01	0.08		0.20	0.21	0.21
28	**4**	0.56	0.04	0.07				
38		0.56	0.07	0.05				
48		0.55	0.06	0.11				
58		0.50	0.05	0.12				
65		0.44	0.05	0.11				
68		0.37	0.04	0.10				
70		0.28	0.07	0.04				

[a] Corresponds to $\bar{\nu}_2$ for minimal $R(\bar{\nu}_2)$.

along the x_1^* axis (ε_{11}^*). The reduced spectra for dyes **1** and **2**, and dye **6**, are very similar to those of dyes **4** and **7**, respectively.

5. Discussion

5.1. *Spectroscopic properties—reduced spectra*

From the results presented in table 2 for unsymmetrically substituted dyes **1** to **4**, it is seen that the q_{22}^* parameter for the band at $\bar{\nu}_1$ is only slightly different from zero. This band is purely polarized in the x_3^+ direction, and $q_{22}^* \neq 0$ means the existence of a small angle between the x_3^+ and x_3^* axes. The largest q_{22}^* and therefore the largest angle has been found for dye **3**, which has a very long alkyl chain attached to the main part of the molecule causing rotation of the molecular long axis.

Looking at the molecular structure of symmetrically substituted dye **5**, it seems that in this case a higher point symmetry group than C_s can be considered, i.e. C_{2V} symmetry. The small value of q_{22}^* for the band at $\bar{\nu}_1$ would confirm that in this case C_{2V} symmetry can be assumed to a good approximation.

From figures 3(*a*) and 3(*b*) it is seen that dyes **1** to **5** have only one purely polarized band connected with the absorption in the visible spectral region. All other bands are characterized by mixed polarization, and the greatest contribution from the polarization along the x_2^* axis always occurs from the band at $\bar{\nu}_2 \approx 38\,000\,\mathrm{cm}^{-1}$.

For dyes **6** and **7**, the point symmetry group C_2 has been assumed. This means that the transition moments related to the bands at various $\bar{\nu}_2$ should lie in the x_1^*, x_2^* plane. Meanwhile, in all the bands, the contribution from the polarization along the x_3^* axis is observed. This can only be explained by the overlapping of various bands at the given $\bar{\nu}_2$. From figure 4(*b*) it is seen that, similarly to the dyes **1** to **5**, only the long wavelength absorption band is purely polarized for dyes **6** and **7**, whereas in all other bands the contributions from polarization along all three x_i^* axes occur.

5.2. *Order parameters*

The results presented in table 4 indicate that the values of the order parameters S^* for the dyes investigated in solution in ZLI 1695 differ significantly from each other,

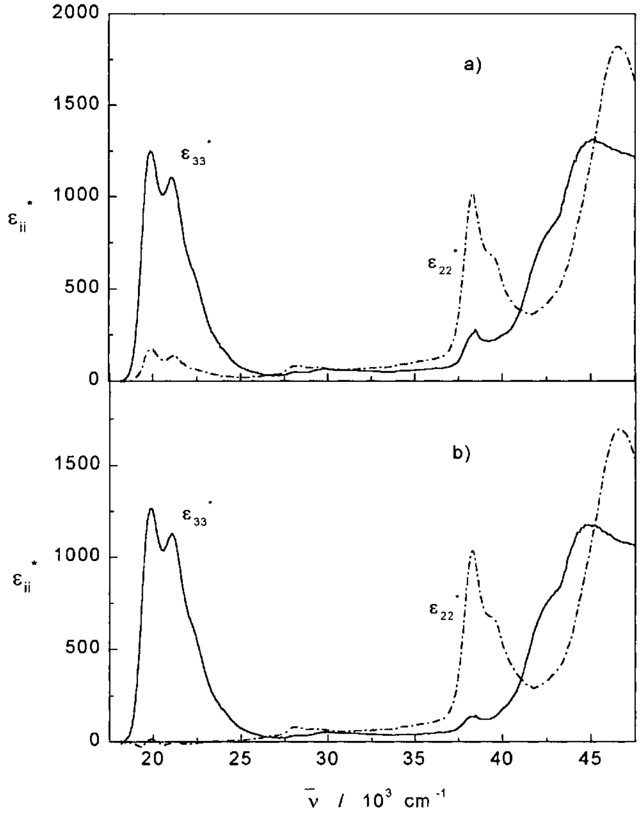


Figure 3. Reduced absorption spectra for dyes in ZLI 1695: (*a*) dye **3**, (*b*) dye **4**. Solid curves ε_{33}^*; dashed curves ε_{22}^*.

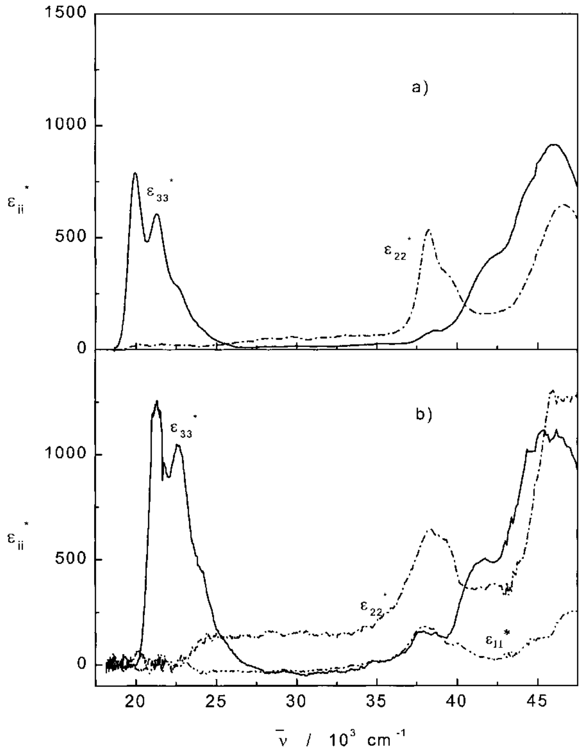


Figure 4. Reduced absorption spectra for dyes in ZLI 1695: (*a*) dye **5**, (*b*) dye **7**. Solid curves ε_{33}^*; dashed curves ε_{22}^*; dotted curve in (*b*) ε_{11}^*.

illustrating the strong influence of the terminal groups, both R_1 and R_2, on S^*. Dye **3**, which has the largest alkyl chain and dye **5**, which has relatively rigid substituents, are the best oriented in the liquid crystal matrix. The symmetrically substituted dyes **6** and **7** are characterized by the smallest S^* values, probably due to steric interactions and the flexibility of the alkyl chains. However, the order parameter rises with increasing chain length. The order parameter S^* for all the dyes under investigation shows a strong dependence on temperature, which is different for the various dyes and demonstrates that the sensitivity of the guest–host mixtures to thermal fluctuations can be very different. The biaxiality parameter D^* for dyes **1** to **5** is rather small and does not differ significantly for the various dyes. For dyes **6** and **7**, the parameter D^* is significantly greater than for the other dyes and at higher temperatures it is comparable with the order parameter S^*. In all cases the D^* values depend very weakly on temperature.

6. Conclusions

The determination of order parameters is of primary importance for both theoretical and experimental aspects, as well as for the technical applications of liquid crystals. The methods used for this purpose are manifold, but it is interesting that the structure of the equations from which the order tensor is evaluated is in many cases the same. Depending on the symmetry of the phase, the number of measurable quantities and the number of elements of the order tensor can change from 25 to 5 if one is handling symmetric tensorial properties. Thus it is important to analyse the information inherent in the experiment. This has been done here especially for UV, Vis and IR methods. Moreover, the order parameters of dyes with symmetry C_2 and C_s have been determined and analysed in terms of general analytical considerations.

Partial support through a Poznan University of Technology Research Project No PB64-002/BW and the 'Fonds der Chemischen Industrie' are gratefully acknowledged. D.B. wishes to thank the Alexander von Humboldt Foundation for financial support during her stay in Kaiserslautern.

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