## Liquid Crystals

## Order parameters from U.V. spectra with incompletely polarized absorption bands

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# Order parameters from U.V. spectra with incompletely polarized absorption bands

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A new method is developed for the determination of Saupe's order parameters $S^*$ and $D^*$ from I.R. or U.V. spectra and the temperature dependence of their degree of anisotropy $R$. This method can be applied to molecules with one uniformly polarized band and another band of mixed polarization if all bands concerned are polarized in the same plane. For that a relation $D^* = f(S^*)$ between the order parameters as a function of temperature is necessary, which can be obtained from the lines of constant entropy in the order triangle. These isentropics are calculated from the orientational distribution function of the ordered system. The resulting function $D^* = f(S^*)$ is equal to that of the mean field theory given by Luckhurst et al., but can be derived here in a very easy way. The method is applied to diaminoanthraquinones with a point symmetry $C_{2v}$.

## 1. Introduction

The I.R. or U.V. spectra of ordered uniaxial systems and their degree of anisotropy $R$ can be described quantitatively by molecular spectroscopic parameters, i.e. the transition moment tensor $\varepsilon_{ij}$ and the two Saupe order parameters $S^*$ and $D^*$ [1, 2]. If the spectroscopic quantities $\varepsilon_{ij}$ are known, then $S^*$ and $D^*$ can be determined from the degree of anisotropy of the anisotropic solution in the case where there are sufficient bands of different polarization. Generally, however, $\varepsilon_{ij}$ is not known in advance and must thus be determined from the same experiment. This determination of $S^*$ and $D^*$ is questionable except when there are sufficient purely polarized absorption bands of different polarization. However, in the U.V. absorption region purely polarized bands are rare, i.e. overlapping bands with different transition moment directions are the rule. Here further information is needed to determine $S^*$ and $D^*$, especially an estimation of the amount of overlapping of the bands. Neglect of this overlap leads to a $D^*$ (sometimes also $S^*$, depending on the type of spectra) which is faulty [2].

For liquid crystal guest–host systems Clark and Saunders [3] and Korte [4] were among the first who tried to handle this problem. For molecules dissolved in polymer sheets, for example, it has been solved by means of a special approximation developed by Thulstrup, Eggers and Michl (T.E.M. model) [5] in order to decompose U.V. spectra into components of different transition moment directions ($\varepsilon_{\beta\beta}$; $\beta = 1, 2, 3$). Last year Strauss and Kuball presented [6] in part a new method for the determination of $S^*$ and $D^*$ from the temperature dependence of the degree of anisotropy $R(\tilde{\nu}, T)$

measured in two different wavenumber regions $\bar{v}_1$ and $\bar{v}_2$ of the spectrum. For this method a relation $R(\bar{v}_2, T) = \phi(R(\bar{v}_1, T))$ was derived in which the function $D^* = f(S^*)$ from the mean field theory developed by Luckhurst and co-workers [7] was used. This method is applicable to molecules with a point symmetry group different from $C_1$, $C_2$, $C_i$, $C_s$ and $C_{2h}$ possessing a spectral region $(\bar{v}_1)$ with only one purely polarized absorption band and a second region $(\bar{v}_2)$ which has a mixed polarization. Furthermore, all bands concerned have to be polarized in the same plane. As an example of application, diaminoanthraquinones were analysed.

In this paper the method is developed further. In particular, the loan from the mean field theory is substituted by a determination of the function $D^* = f(S^*)$ from the curves of constant entropy in the order triangle. The procedure is applied to evaluate the order parameters $S^*$ and $D^*$ of diaminoanthraquinones of symmetry $C_{2v}$ where the orientation axis is fixed by symmetry.

## 2. Theoretical background

The degree of anisotropy, available from the anisotropic absorption of light, is defined by

$$R = (\varepsilon_1 - \varepsilon_2)/3\varepsilon_{\text{iso}}, \tag{1}$$

where $\varepsilon_1$ and $\varepsilon_2$ are the molar decadic absorption coefficients for light polarized parallel and perpendicular to the optical axis of a uniaxial system, respectively, and $\varepsilon_{\text{iso}} = \frac{1}{3}(\varepsilon_1 + 2\varepsilon_2)$ is the absorption coefficient of the isotropic state. The Saupe order parameters $S$ and $D$ depend on the molecule-fixed coordinate system chosen. Two different coordinate systems ($x_i^+$ and $x_i^*$) have a distinct significance in connecting the order parameters with the absorption coefficients and the degree of anisotropy. The coordinates $x_i^+$ refer to the principal axes of the transition moment tensor $\varepsilon_{ij}$ and the $x_i^*$ to those of the orientational distribution tensor $g_{ij33}$. The order parameters are then indicated as $S^+$, $D^+$ and $S^*$, $D^*$, respectively. Whereas, in general, the quantities $\varepsilon_\beta$ ($\beta = 1, 2$) as well as $R$ depend on non-diagonal elements of $\varepsilon_{ij}$ and $g_{ij33}$, in the description with $x_i^+$ or $x_i^*$ only diagonal elements enter $\varepsilon_\beta$ as well as $R$ because $\varepsilon_{ij}$ or $g_{ij33}$ is diagonal. Therefore, the degree of anisotropy can be expressed as

$$R = \frac{1}{2}(3q_{33}^\# - 1)S^* + \frac{3^{1/2}}{2}(q_{22}^\# - q_{11}^\#)D^*, \tag{2a}$$

where

$$q_{\beta\beta}^\# = \frac{\varepsilon_{\beta\beta}^\#}{\sum\limits_{i=1}^{3} \varepsilon_{ii}^\#}, \quad (0 \leqslant q_{\beta\beta}^\# \leqslant 1) \tag{2b}$$

and # stands for + or *. The order parameters are defined by

$$S^\# = \tfrac{1}{2}(3g_{3333}^\# - 1), \tag{3a}$$

$$D^\# = \frac{3^{1/2}}{2}(2g_{2233}^\# + g_{3333}^\# - 1), \tag{3b}$$

where

$$g_{ijkl}^\# = \frac{1}{4\pi}\int f^\#(\beta, \gamma)\, a_{ik}a_{jl} \sin\beta\, d\beta\, d\gamma. \tag{4}$$
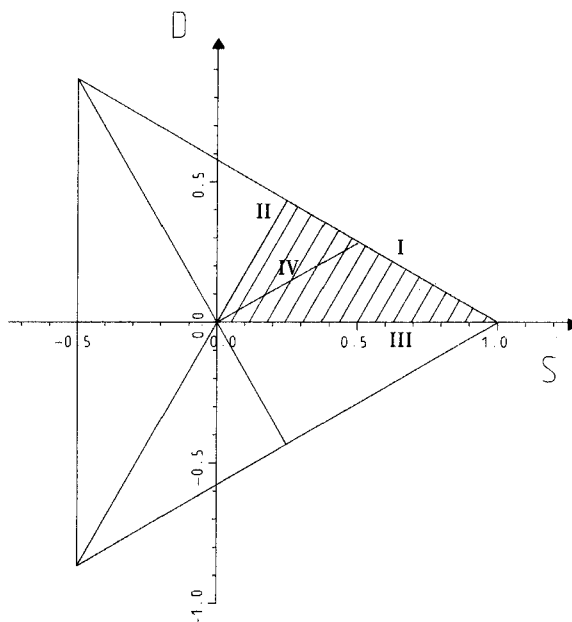
Figure 1. Order triangle. The hatched area is sufficient to describe the order of a uniaxial system $(S, D) \rightarrow (S^*, D^*)$. The five remaining triangles bear the same information but belong to the principal axes of the orientational distribution tensor with a changed numbering. The straight lines I–IV characterize special relations between $S^*$ and $D^*$: I, $D^* = 3^{-1/2}(1 - S^*)$; II, $D^* = 3^{1/2}S^*$; III, $D^* = 0$; IV, $D^* = 3^{-1/2}S^*$.

$f^*(\beta, \gamma)$ is the orientational distribution function for a uniaxial system with the optical axis parallel to the space-fixed $x_3'$ axis. The $a_{ij}$ are the elements of the orthogonal transformation matrix from the space-fixed $(x_i')$ to the molecule-fixed $(x_i^\#)$ coordinate system. The convention for the numbering of the eigenvalues of $g_{ij33}$, $g_{3333}^* \geqslant g_{2233}^* \geqslant g_{1133}^*$ has the consequence $S^* \geqslant S$ for a given orientational distribution and an arbitrary molecule-fixed coordinate system. The 'orientation axis' is defined as the $x_3^*$ axis. Except for the molecules with a point symmetry group $C_1$, $C_2$, $C_i$, $C_s$ or $C_{2h}$, the axes of the $(x_i^+)$ and the $(x_i^*)$ systems coincide. The orientation axis is fixed by symmetry and the above convention for numbering the eigenvalues of $g_{ij33}$. The numbering of the $x_i^+$ with respect to the $x_i^*$ is arbitrary. Figure 1 shows the 'order triangle' referring to parameters $S$ and $D$. The hatched region $(S^*, D^*)$ is sufficient to describe the order of a uniaxial system, i.e. every possible function $f^*(\beta, \gamma)$ has an image point in this region.

## 3. Working equations
### 3.1. *The basic relation*

For the analysis we restrict ourselves to systems where the axes of the $(x_i^+)$ and the $(x_i^*)$ coordinate system coincide by symmetry. Furthermore, we assume all absorption bands concerned to be polarized in the same plane (the plane of a molecule with a $\pi$-system, for example) and, moreover, that there is one absorption region $(\bar{\nu}_1)$ with a purely polarized band and another $(\bar{\nu}_2)$ where bands of different polarization directions overlap (mixed polarization). The degree of anisotropy of the first region can then, as a function of temperature, be compared with that of the second region.

From equations (2),

$$R(\bar{v}_1, T) = \frac{1}{2}[3q_{33}^*(\bar{v}_1) - 1]S^*(T) + \frac{3^{1/2}}{2}[q_{22}^*(\bar{v}_1) - q_{11}^*(\bar{v}_1)]D^*(T), \quad (5a)$$

$$R(\bar{v}_2, T) = \frac{1}{2}[3q_{33}^*(\bar{v}_2) - 1]S^*(T) + \frac{3^{1/2}}{2}[q_{22}^*(\bar{v}_2) - q_{11}^*(\bar{v}_2)]D^*(T), \quad (5b)$$

and a function $D^* = f(S^*)$, derived in §3.5, there follows the relation

$$R(\bar{v}_2, T) = \Phi(R(\bar{v}_1, T)). \quad (6)$$

The elimination of $S^*$ from equations (5) yields

$$R(\bar{v}_2, T) = A(\bar{v}_2)R(\bar{v}_1, T) + B(\bar{v}_2)D^*(T). \quad (7)$$

The coefficients $A(\bar{v}_2)$ and $B(\bar{v}_2)$ depend on the $q_{\beta\beta}^*(\bar{v}_2)$. The plane of $R(\bar{v}_1, T)$ and $R(\bar{v}_2, T)$ as cartesian coordinates will be used in the later discussion. There are six different pairs of coefficients, as listed in table 1. This results from the different possibilities of placing the principal axes $x_i^*$ of $g_{ij33}$ relative to the molecular geometry as shown in figure 2.
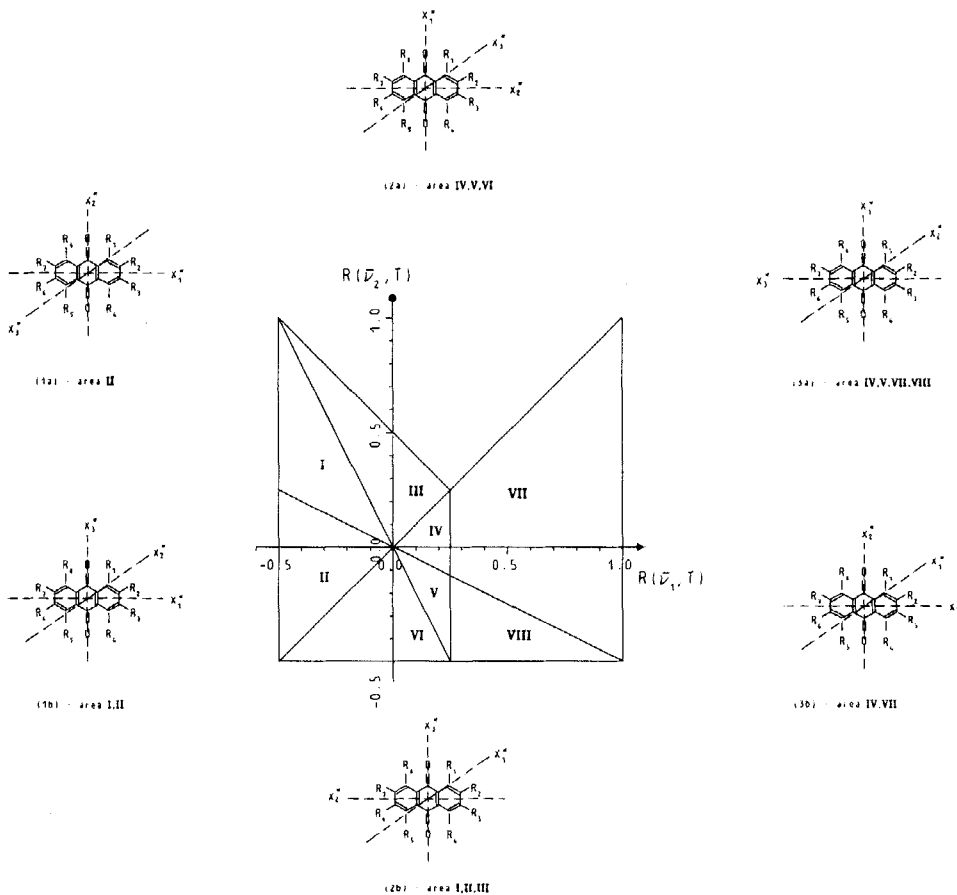


Figure 2.   Assignment of the coordinates of the transition moment tensor $\varepsilon_{ij}^+$ to the $x_i^*$ coordinate system with $g_{3333}^* \geqslant g_{2233}^* \geqslant g_{1133}^*$.

Table 1. The coefficients $A(\bar{v}_2)$ and $B(\bar{v}_2)$ of equation (7).

| No. | Molecular plane | $q_{\beta\beta}^*$ for the transition | | $A(\bar{v}_2)$ | $B(\bar{v}_2)$ |
|---|---|---|---|---|---|
| | | Purely polarized† | Mixed polarized‡ | | |
| 1a | 1,2 | $q_{11}^*(\bar{v}_1) = 1$ | $q_{22}^*(\bar{v}_2) \neq 0;\quad q_{11}^*(\bar{v}_2) \neq 0$ | 1 | $3^{1/2}q_{22}^*(\bar{v}_2)$ |
| 1b | 1,3 | $q_{11}^*(\bar{v}_1) = 1$ | $q_{33}^*(\bar{v}_2) \neq 0;\quad q_{11}^*(\bar{v}_2) \neq 0$ | $1 - 3q_{33}^*(\bar{v}_2)$ | $-3^{1/2}q_{33}^*(\bar{v}_2)$ |
| 2a | 1,2 | $q_{22}^*(\bar{v}_1) = 1$ | $q_{11}^*(\bar{v}_2) \neq 0;\quad q_{22}^*(\bar{v}_2) \neq 0$ | 1 | $-3^{1/2}q_{11}^*(\bar{v}_2)$ |
| 2b | 2,3 | $q_{22}^*(\bar{v}_1) = 1$ | $q_{33}^*(\bar{v}_2) \neq 0;\quad q_{22}^*(\bar{v}_2) \neq 0$ | $1 - 3q_{33}^*(\bar{v}_2)$ | $3^{1/2}q_{33}^*(\bar{v}_2)$ |
| 3a | 1,3 | $q_{33}^*(\bar{v}_1) = 1$ | $q_{11}^*(\bar{v}_2) \neq 0;\quad q_{33}^*(\bar{v}_2) \neq 0$ | $1 - \tfrac{3}{2}q_{11}^*(\bar{v}_2)$ | $-\tfrac{1}{2}3^{1/2}q_{11}^*(\bar{v}_2)$ |
| 3b | 2,3 | $q_{33}^*(\bar{v}_1) = 1$ | $q_{22}^*(\bar{v}_2) \neq 0;\quad q_{33}^*(\bar{v}_2) \neq 0$ | $1 - \tfrac{3}{2}q_{22}^*(\bar{v}_2)$ | $\tfrac{1}{2}3^{1/2}q_{22}^*(\bar{v}_2)$ |

† $\bar{v}_1$ = wavenumber of the purely polarized transition.

‡ $\bar{v}_2$ = wavenumber in the region of mixed polarization; the first column gives the main contribution in this spectral region.

### 3.2. *Relating the transition moment directions to the $x_i^*$ axes by the $R(\bar{v}_1)$, $R(\bar{v}_2)$ plane*

In order to simplify the simulation of the function $R(\bar{v}_2, T) = \Phi(R(\bar{v}_1, T))$, as described later, it is possible to restrict the number of cases, given in table 1, by a purely qualitative procedure. The function $R(\bar{v}_2, T) = \Phi(R(\bar{v}_1, T))$ is confined to certain regions in the $R(\bar{v}_1)$, $R(\bar{v}_2)$ plane for the different cases because of the following restrictions on the $q_{\beta\beta}^*$, $S^*$ and $D^*$ values

$$0 \leqslant q_{\beta\beta}^* \leqslant 1, \qquad 0 \leqslant S^* \leqslant 1, \tag{8a}$$

$$\left.\begin{array}{ll} 0 \leqslant D^* \leqslant 3^{1/2}S^*, & \text{for } 0 \leqslant S^* \leqslant \tfrac{1}{4}; \\[4pt] 0 \leqslant D^* \leqslant 3^{-1/2}(1 - S^*), & \text{for } \tfrac{1}{4} \leqslant S^* \leqslant 1. \end{array}\right\} \tag{8b}$$

Some of the six situations of table 1 are compatible with several regions of figure 2. However, in these cases the sign of the curvature of $R(\bar{v}_2, T) = \Phi(R(\bar{v}_1, T))$ allows a further differentiation as will be discussed in §3.3.

In order to get a good understanding of figure 2 one has to go into further details. We will therefore inspect the areas IV and VII resulting from equation (7) and the coefficients of the situation 3b in table 1 and figure 2. Since $BD^* \geqslant 0$, the lower bound (lb) of $R(\bar{v}_2, T)$ is given here by

$$[R(\bar{v}_2, T)]_{\text{lb}} = [1 - \tfrac{3}{2}q_{22}^*(\bar{v}_2)]R(\bar{v}_1, T). \tag{9}$$

In order to calculate the upper bound of $R(\bar{v}_2, T)$, the faces of the order triangle (figure 1)

$$D^* = 3^{1/2}S^* = 3^{1/2}R(\bar{v}_1, T), \quad \text{for } 0 \leqslant S^* \leqslant \tfrac{1}{4} \tag{10a}$$

and

$$D^* = 3^{-1/2}(1 - S^*) = 3^{-1/2}[1 - R(\bar{v}_1, T)], \quad \text{for } \tfrac{1}{4} \leqslant S^* \leqslant 1 \tag{10b}$$

have to be used. Insertion of equations (10) into equation (7) yields, for the upper bound (ub),

$$[R(\bar{v}_2, T)]_{\text{ub}} = R(\bar{v}_1, T), \quad \text{for } 0 \leqslant S^* = R(\bar{v}_1, T) \leqslant \tfrac{1}{4} \tag{11a}$$
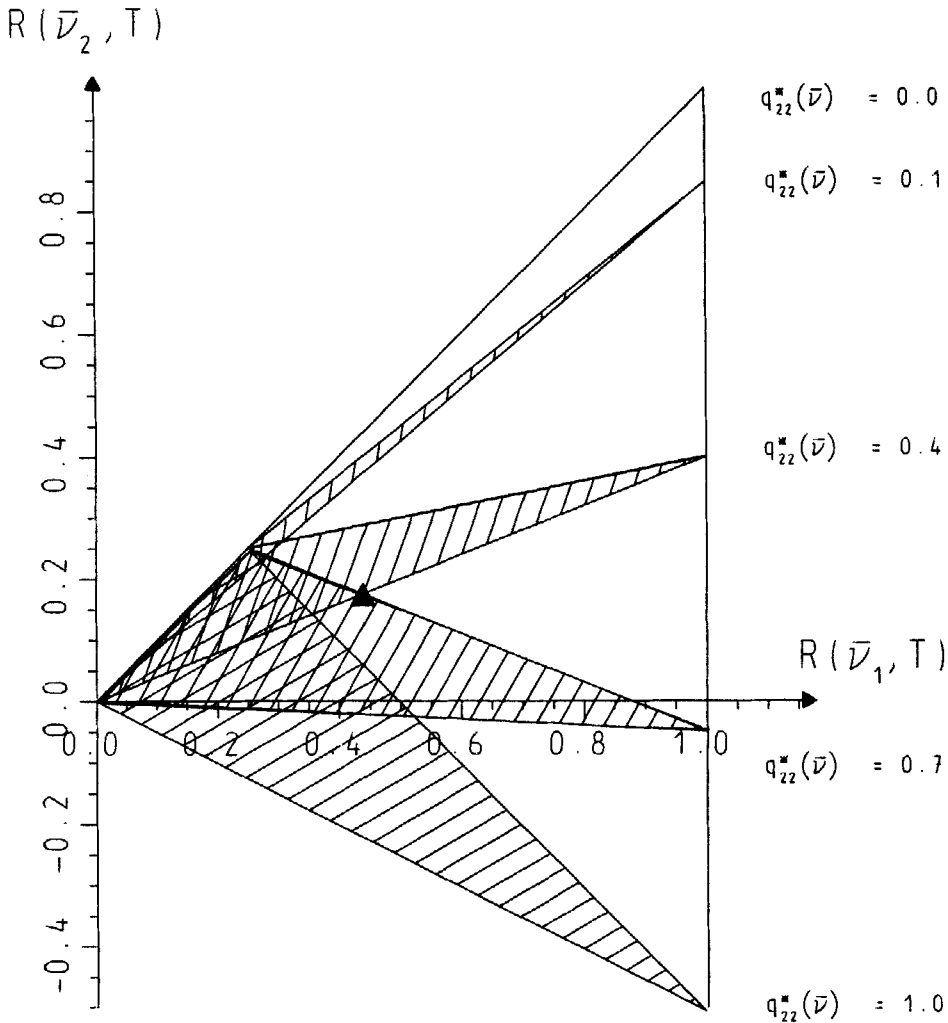
Figure 3. Constructing scheme for the areas IV and VII. The hatched areas represent possible regions of the curve given by equation (6) for special $q_{22}^*(\bar{v}_2)$ values as given at the right ordinate. For the experimental point ▲ an upper and lower bound of $D^*$ can be estimated by the upper face of the triangle corresponding to $q_{22}^*(\bar{v}_2) = 0.7$ and the lower face of the triangle corresponding to $q_{22}^*(\bar{v}_2) = 0.4$.

and

$$[R(\bar{v}_2, T)]_{ub} = [1 - 2q_{22}^*(\bar{v}_2)]R(\bar{v}_1, T) + \tfrac{1}{2}q_{22}^*(\bar{v}_2), \quad \text{for } \tfrac{1}{4} \leqslant S^* = R(\bar{v}_1, T) \leqslant 1.$$

$$(11\,b)$$

Equations (9) and (11) describe straight lines which enclose a triangle shown in figure 3 for the values $q_{22}^*(\bar{v}_2) = 0.1, 0.4, 0.7$ and 1. For given $q_{22}^*(\bar{v}_2)$ value, all points satisfying $R(\bar{v}_2, T) = \Phi(R(\bar{v}_1, T))$ lie within this triangle which is covered when $S^*$ and $D^*$ in equations (5) vary over the hatched region in figure 1. In the case of $q_{22}^*(\bar{v}_2) = \tfrac{2}{3}$ the triangle corresponds to the order triangle if the ordinate is multiplied by the factor $3^{1/2}[R(\bar{v}_1, T) = S^*, R(\bar{v}_2, T) = 3^{-1/2}D^*]$. The additional variation of

$q_{22}^*(\bar{v}_2)$ yields the areas IV and VII. If $q_{22}^*(\bar{v}_2)$ approaches zero, then the triangle degenerates into a line. The determination of the $D^*$ value from experiment then becomes impossible. This can easily be understood from the special spectroscopic situation of this case, since for $q_{22}^*(\bar{v}_2) = 0$ the transitions used $(\bar{v}_1, \bar{v}_2)$ are polarized parallel to each other, i.e. the molecule appears as a line to the interacting light wave. It is interesting to remark that for $D^* = 0$ the experiment must yield a straight line and vice versa, i.e. if the $R(\bar{v}_2, T)$, $R(\bar{v}_1, T)$-dependence has the form of a straight line, one can conclude $D^* = 0$ unequivocally except for $q_{22}^*(\bar{v}_2) = 0$, which means that $B(\bar{v}_2) = 0$.

### 3.3. *Differentiation by the sign of curvature of* $R(\bar{v}_2, T) = \Phi(R(\bar{v}_1, T))$

For $D^* = 0$, equation (7) yields a straight line. Because $D^* \geqslant 0$ and $q_{\beta\beta}^* \geqslant 0$, the term $BD^*$ is positive for the situations $1\,a$, $2\,b$ and $3\,b$ and negative for $1\,b$, $2\,a$ and $3\,a$. Therefore, $BD^*$ is added to the ordinate values of the straight line in the first three cases, and thus the values of $R(\bar{v}_2, T)$ are above $R(\bar{v}_2, T) = A(\bar{v}_2)R(\bar{v}_1, T)$, whereas for $1\,b$, $2\,a$ and $3\,a$ they are below this line. For $S^* \to 0$ or $S^* \to 1$ they converge to this line again, because then $D^* \to 0$. The curve given by equation (6) is convex from above for the situation $3\,b$ and concave from above for $3\,a$. The other situations are more complicated than $3\,a$ and $3\,b$ because for $1\,a$, $b$ and $2\,a$, $b$ $\frac{1}{2}3^{1/2}[q_{22}^*(\bar{v}_1) - q_{11}^*(\bar{v}_1)] \neq 0$ and thus $R(\bar{v}_1, T)$, according to equation (5 $a$), contains not only $S^*$ but also $D^*$. This will be discussed in a subsequent paper in the context of further experimental results. For situations $3\,a$ and $3\,b$ the largest difference between the values of $R(\bar{v}_2, T)$ and the straight line should, according to equation (7), be near the maximum of the $D^* = f(S^*)$ curve, i.e. at about $S^* = R(\bar{v}_1, T) \approx 0 \cdot 4$. With $D^* = f(S^*)$, as shown later in figure 8, the $R(\bar{v}_2, T)$, $R(\bar{v}_1, T)$-dependence yields numerical results for the situations $2\,b$ and $3\,b$ as shown in figures 4 and 5. The assignment of the situations corresponding to the areas I–VIII to a special experimental case, i.e. the transition moment tensor and by this of the $x_i^*$ axes to the molecular framework, can be derived from table 2 together with figure 2.

The assignment is unequivocal if the temperature dependence of $R(\bar{v}, T)$ is strong, i.e. if the curve $R(\bar{v}_2, T) = \Phi(R(\bar{v}_1, T))$ extends over a large range in the $R(\bar{v}_1)$, $R(\bar{v}_2)$ plane and if it is not a straight line. If $D^*$ is very small, and thus the curve is nearly a straight line, then the assignment is uncertain. To overcome this problem, one may choose another wavenumber region for measuring $R(\bar{v}_2, T)$ because the curvature of the curves is changed by changing the $q_{\beta\beta}^*(\bar{v}_2)$.

Table 2. Assignment of the situations $1\,a$–$3\,b$ to the coordinates of the transition moment tensor by the type of curves and their position in the different areas of figure 2.

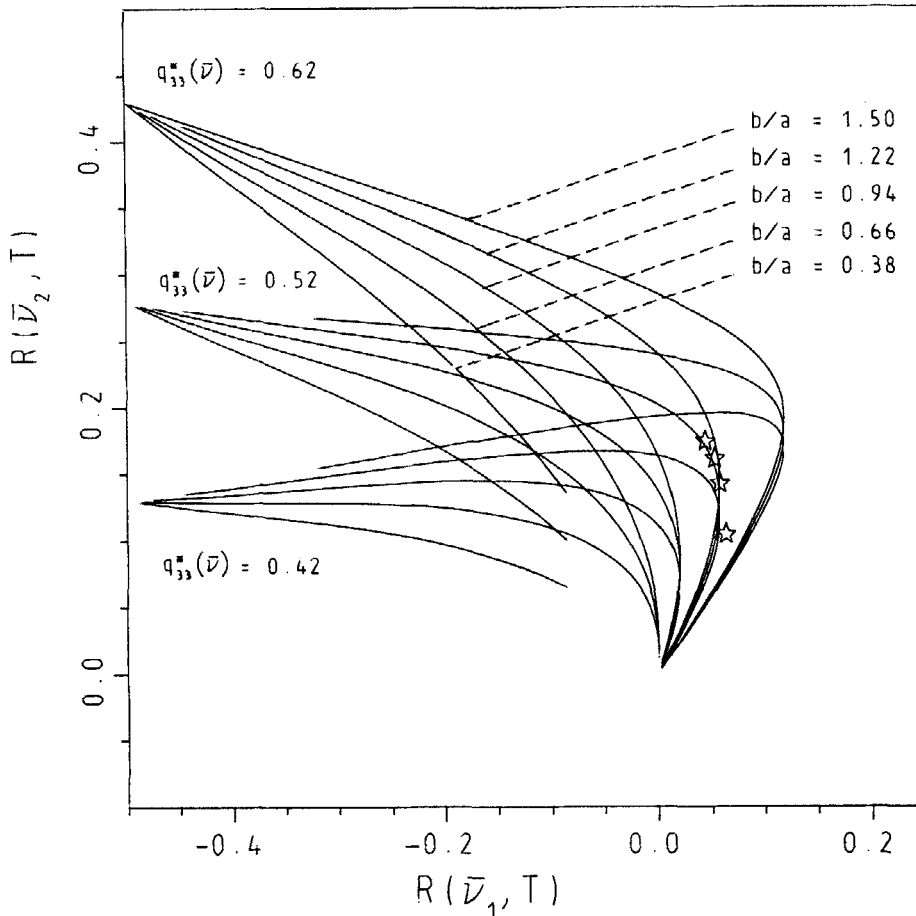| Curve | Situation | | | | | |
| | $1\,a$ | $1\,b$ | $2\,a$ | $2\,b$ | $3\,a$ | $3\,b$ |
| --- | --- | --- | --- | --- | --- | --- |
| Below the straight line ($D^* = 0$) | | I, II | IV, V, VI | | IV, VI VII, VIII | |
| Above the straight line ($D^* = 0$) | II | | | I, II, III | | IV, VII |

Figure 4.　Simulation of the $R(\bar{v}_2, T)$, $R(\bar{v}_1, T)$-dependence for the situation $2\,b$.

### 3.4. *Confinement of the $D^*$ values by approximated $q_{22}^*(\bar{v}_2)$ values for the situation 3 b as an example*

An experimentally obtained point in the $R(\bar{v}_1)$, $R(\bar{v}_2)$ plane, as indicated by the ▲ in figure 3, belongs to infinitely many triangles determined by different $q_{22}^*(\bar{v}_2)$ values (right ordinate). However, there are two special triangles where the point lies on the upper or lower face, respectively. From these a lower bound $[q_{22}^*(\bar{v}_2)]_{lb}$ and an upper bound $[q_{22}^*(\bar{v}_2)]_{ub}$ can be determined by which the interval of the $D^*$ values resulting from the order triangle (see equations 8) can be restricted. This restriction can be used to check the $D^*$ values calculated by the method given in §3.6.

### 3.5. *Isentropics in the order triangle and the relation $D^* = f(S^*)$*

Every point in the order triangle (figure 1) is an image point of orientational distribution functions and thus represents some kind of order. If higher order parameters are neglected, the order of a system is completely described by $S^*$ and $D^*$. When comparing different states of one or several molecular systems, e.g. liquid crystal guest–host systems, the question of whether a large $S^*$ and a small $D^*$ or
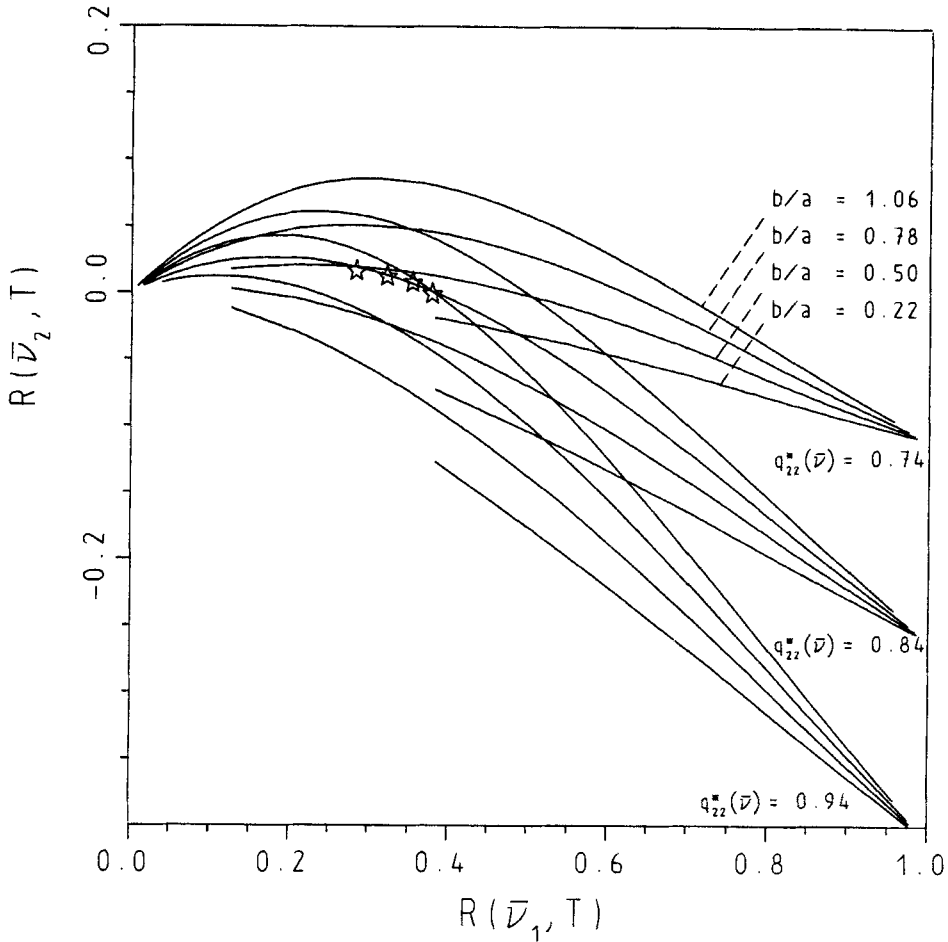
Figure 5. Simulation of the $R(\bar{\nu}_2, T)$, $R(\bar{\nu}_1, T)$-dependence for the situation $3b$.

vice versa represents the state of higher order arises. In other words, a measure of order is necessary in which both quantities are taken into account. As is known well from statistical thermodynamics, this measure is provided by the entropy. For the present as well as other purposes it is useful to calculate the lines of constant entropy (isentropics) $\mathscr{S}(S^*, D^*) = $ constant in the order triangle. (In order to avoid confusion with the order parameter $S$, we denote the entropy by a script letter.)

The starting point for the calculation is the partition function $Z = Z_M^N$ of the system of $N$ molecules at temperature $T$ where $Z_M$ is the partition function of a single molecule and only the rotational degrees of freedom are concerned. If the potential energy of a guest molecule produced by its surroundings, i.e. the host, is $U(\alpha, \beta, \gamma)$ with the Eulerian angles $\alpha$, $\beta$ and $\gamma$, and if its kinetic energy is neglected, the partition function is

$$Z_M = \int \exp\left(-\frac{U(\alpha, \beta, \gamma)}{kT}\right) \sin\beta \, d\alpha \, d\beta \, d\gamma, \tag{12}$$

where the integrand is proportional to the orientational distribution function

$$f(\alpha, \beta, \gamma) = \frac{8\pi^2}{Z_M} \exp\left(-\frac{U(\alpha, \beta, \gamma)}{kT}\right). \tag{13}$$

Now we assume a uniaxial system with the symmetry axis in the $x_3'$ direction and, furthermore, the following symmetry properties of its orientational distribution function $f(\beta, \gamma)$:

$$f^*(\beta, \gamma) \;=\; f^*(\beta, \gamma + \pi) \;=\; f^*(\beta, -\gamma) \;=\; f^*(\pi - \beta, \gamma). \tag{14}$$

As a consequence, the tensor $g_{ij33}$ is diagonal, so the designation $f^*$ is justified. Furthermore, the expansion of $U(\beta, \gamma)$ into spherical harmonics $Y_{lm}(\beta, \gamma)$ up to $l = 2$ contains, apart from an irrelevant additive constant, only two independent parameters and may be written as

$$U(\beta, \gamma) \;=\; \frac{a}{2}\,(3\cos^2\beta \,-\, 1) \;-\; \frac{3^{1/2}}{2}\,b\sin^2\beta\cos 2\gamma. \tag{15}$$

We choose the values of $a$ and $b$ in such a way that $U(\beta, \gamma)$ has a minimum at $\beta = 0$ (and thus also at $\beta = \pi$) for all values of $\gamma$, i.e. $a < 0$ and $|b| < 3^{1/2}|a|$.

The Helmholtz free energy per molecule

$$F(T, a, b) \;=\; -kT\ln Z_{\mathrm{M}}(T, a, b) \tag{16}$$

as a function of $T$ and the 'external variables' $a$ and $b$ yields all desired thermodynamic quantities and relations. The entropy per molecule of the orientational distribution is

$$\mathscr{S} \;=\; -\left(\frac{\partial F}{\partial T}\right)_{a,b} \;=\; \mathscr{S}\left(\frac{a}{T}, \frac{b}{T}\right). \tag{17}$$

The last form follows directly from equations (16), (12) and (15). Analogously one obtains, according to their definition by equations (3) and (4), the order parameters

$$S^* \;=\; \left(\frac{\partial F}{\partial a}\right)_{T,b} \;=\; S^*\left(\frac{a}{T}, \frac{b}{T}\right), \tag{18a}$$

$$D^* \;=\; \left(\frac{\partial F}{\partial b}\right)_{T,a} \;=\; D^*\left(\frac{a}{T}, \frac{b}{T}\right), \tag{18b}$$

which appear here as internal variables of the system, as should be. Because $F$ is homogeneous of the first degree in the variables $a$, $b$ and $T$, according to Euler's theorem

$$F \;=\; aS^* + bD^* - T\mathscr{S} \tag{19}$$

holds, from which the energy per molecule of the system results in

$$E \;=\; F + T\mathscr{S} \;=\; aS^* + bD^*. \tag{20}$$

Equations (20), (18) and (17) yield

$$dE \;=\; dF + T\,d\mathscr{S} + \mathscr{S}\,dT \;=\; S^*\,da + D^*\,db + T\,d\mathscr{S}, \tag{21}$$

and comparison with the differential of the right-hand side of equation (20) shows that

$$T\,d\mathscr{S} \;=\; a\,dS^* + b\,dD^*. \tag{22}$$

Elimination of $a/T$ and $b/T$ from equations (17) and (18) gives

$$\mathscr{S} \;=\; \mathscr{S}(S^*, D^*), \tag{23}$$

which does not depend explicitly on the temperature and yields the desired isentropics $\mathscr{S}(S^*, D^*) = $ constant drawn in figure 6. According to equation (22) the slope of the isentropic $(d\mathscr{S} = 0)$ at a point with coordinates $S^*(a/T, b/T)$, $D^*(a/T, b/T)$ is

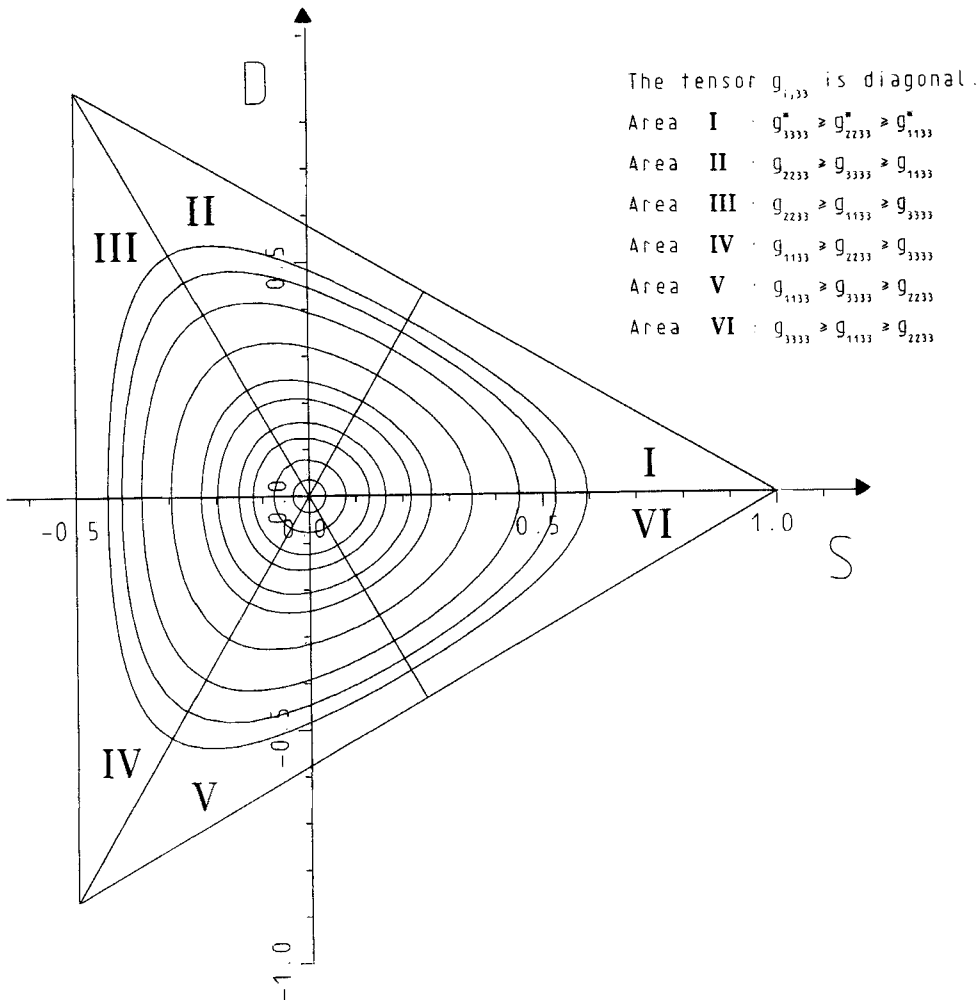$$\frac{dD^*}{dS^*} \;=\; -\frac{a}{b}. \tag{24}$$

The tensor $g_{i,jj}$ is diagonal.

Area I : $g_{3333}^{*} \geqslant g_{2233}^{*} \geqslant g_{1133}^{*}$

Area II : $g_{2233} \geqslant g_{3333} \geqslant g_{1133}$

Area III : $g_{2233} \geqslant g_{1133} \geqslant g_{3333}$

Area IV : $g_{1133} \geqslant g_{2233} \geqslant g_{3333}$

Area V : $g_{1133} \geqslant g_{3333} \geqslant g_{2233}$

Area VI : $g_{3333} \geqslant g_{1133} \geqslant g_{2233}$

Figure 6. The isentropics $\mathscr{S}(S^{*}, D^{*}) = $ constant in the order triangle (relative entropy units from inside outwards: 1·000, 0·997, 0·992, 0·986, 0·975, 0·964, 0·937, 0·895, 0·854 and 0·813).

On the other hand, equations (18) yield, for fixed values of $a$ and $b$, the variation of $S^{*}$ and $D^{*}$ with temperature which is shown by a curve in figure 7. Elimination of $T$ would give the equation of this curve; for example, in the form

$$D^{*} = f(S^{*}, b/a). \qquad (25)$$

It intersects all isentropics in points where the slope of the latter has the same value $-a/b$. By this property it can be constructed from the isentropics according to figure 7†.

† In general, $a$ and $b$ are functions of temperature determined by the host system. In this case, for the last statement to hold, $b/a$ has to be independent of temperature, which is to be expected from mean field theory [7] and proves to be true within the experimental errors in the cases considered here, as can be seen from the consistency of the evaluation of our experimental data.
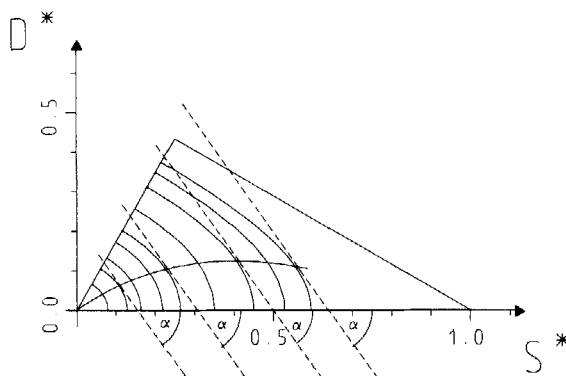
Figure 7.    Construction of the function $D^* = f(S^*, b/a)$ from the isentropics.

For the limiting cases of very high and very low temperatures equations (18) and (17) take on a simple form. The results are:

(a) for very high temperatures

$$Z_M = 8\pi^2 \left(1 + \frac{a^2 + b^2}{10(kT)^2}\right) \tag{26}$$

and thus

$$S^* = -\frac{a}{5kT}, \qquad D^* = -\frac{b}{5kT}, \tag{27}$$

$$\mathscr{S} = k[\ln 8\pi^2 - \tfrac{5}{2}(S^{*2} + D^{*2})]; \tag{28}$$

(b) for very low temperatures

$$Z_M = \frac{8\pi^2}{(9a^2 - 3b^2)^{1/2}} kT \exp\left(-\frac{a}{kT}\right), \tag{29}$$

whence

$$S^* = 1 + \frac{3a}{3a^2 - b^2} kT, \qquad D^* = -\frac{b}{3a^2 - b^2} kT, \tag{30}$$

$$\mathscr{S} = k\left\{1 + \ln\frac{8\pi^2}{3} + \frac{1}{2}\ln[(1 - S^*)^2 - 3D^{*2}]\right\}. \tag{31}$$

In the first case the isentropics are circles with centres at $S^* = D^* = 0$ and the curves given by equation (25) are radii of these circles. In the second case the isentropics are hyperbolae with centres at $S^* = 1$, $D^* = 0$ and the faces $D^* = \pm 3^{-1/2}(1 - S^*)$ of the orientation triangle as asymptotes. The curves corresponding to equation (25) are straight lines through the point (1, 0).

### 3.6. *Performance of the method*

The starting point is the degree of anisotropy $R(\bar{v}, T)$ measured as a function of temperature for two wavenumbers $\bar{v}_1$ and $\bar{v}_2$ (figure 8), i.e. an experimental curve $R(\bar{v}_2, T) = \Phi(R(\bar{v}_1, T))$ is measured. This curve is fitted by calculating $R(\bar{v}_1, T)$ and $R(\bar{v}_2, T)$ from equations (5) and (25) with varying parameters $q_{\beta\beta}^*(\bar{v}_2)$ and $b/a$. For the best fit of the experimental result the sum of the squares of the deviations of the
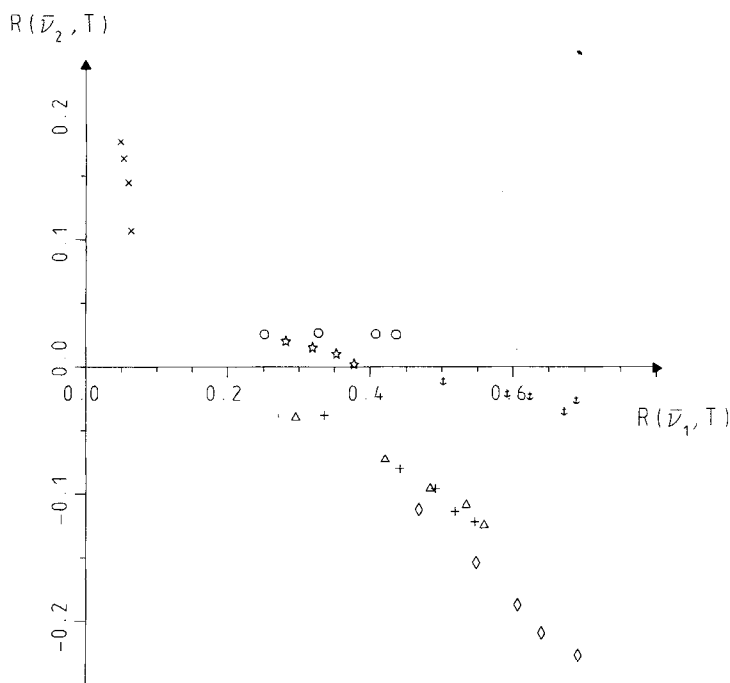
Figure 8.　The $R(\bar{v}_2, T)$, $R(\bar{v}_1, T)$-dependence of dyes 1–7 in ZLI 1695 (Merck) as a host (temperature region from 28 to 68°C; for symbols, see table 4).

experimental points from the theoretical curve is a minimum. The results are controlled by looking at the fitted curve with respect to the measured points, as shown for dyes **2** and **4** in figures 4 and 5. From the fitted curve $R(\bar{v}_2, T) = \Phi(R(\bar{v}_1, T))$, $q_{\beta\beta}^*(\bar{v}_2)$ is taken in order to calculate $S^*$ and $D^*$ from equations (5) for various temperatures. From $S^*$, $D^*$ and the measured degree of anisotropy, the reduced spectra, i.e. the tensor coordinates $\varepsilon_{\beta\beta}$ ($\beta = 1, 2, 3$), can be evaluated. For the whole method $q_{\beta\beta}^*(\bar{v})$ is assumed to be independent of temperature, i.e. solute–solvent interaction and variation of conformations have no influence in the temperature interval used.

## 4.　Results

For the dyes given in table 3, $R(\bar{v}, T)$ has been measured in the host system ZLI 1695 (Merck) in the temperature region from 28 to 68°C. As can be seen in figure 8, the slopes of the curves equation (6) indicated by the measured points and the areas corresponding to figure 2 are very different for the different compounds. Figure 9 shows the calculated function $D^* = f(S^*)$ for dyes 1–7. The results for $q_{\beta\beta}(\bar{v}_2)$, $b/a$, $S^*$ and $D^*$ for these compounds are summarized in table 4. Furthermore, for **6** as an example, the reduced spectra calculated with $q_{22}^*$ from table 4 are compared with the spectra calculated by the T.E.M. model and the approximation where $q_{22}^* = 1$ (figure 10).

## 5.　Discussion

If a molecular system has two purely polarized transitions with orthogonal transition moment directions, then the order parameters $S^*$ and $D^*$ can be calculated
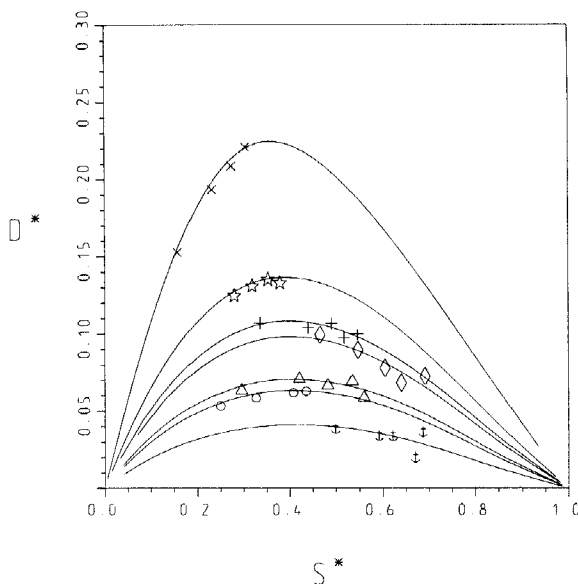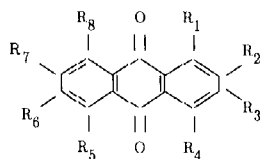
Figure 9. The relation $D^* = f(S^*)$ between the order parameters as a function of temperature (temperature region from 28 to 68°C; for symbols, see table 4).

Table 3. Anthraquinone dyes.



| No. | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | $R_6$ | $R_7$ | $R_8$ |
|-----|-------|-------|-------|-------|-------|-------|-------|-------|
| 1 | $NH_2$ | H | H | H | H | H | H | $NH_2$ |
| 2 | NH-⟨⟩-$CH_3$ | H | H | H | H | H | H | NH-⟨⟩-$CH_3$ |
| 3 | $NH_2$ | $CH_2$-⟨⟩ | H | H | H | H | $CH_2$-⟨⟩ | $NH_2$ |
| 4 | $NH_2$ | ⟨⟩— | H | H | H | H | ⟨⟩— | $NH_2$ |
| 5 | $NH_2$ | Br | H | H | H | H | Br | $NH_2$ |
| 6 | $NH_2$ | ⟨⟩ | H | H | H | H | ⟨⟩ | $NH_2$ |
| 7 | $NH_2$ | ⟨⟩ | H | ⟨⟩ | ⟨⟩ | H | ⟨⟩ | $NH_2$ |

directly because there is sufficient experimental information. This condition is not often fulfilled for U.V. spectra. If there are only bands of mixed polarization, determination of $S^*$ and $D^*$ is possible only by a very rough approximation. For molecules with one purely polarized transition ($\bar{\nu}_1$) and a second spectral region ($\bar{\nu}_2$) with overlapping bands, Saupe's order parameters can be determined from the temperature dependence of the degree of anisotropy $R(\bar{\nu}, T)$, measured in these two spectral
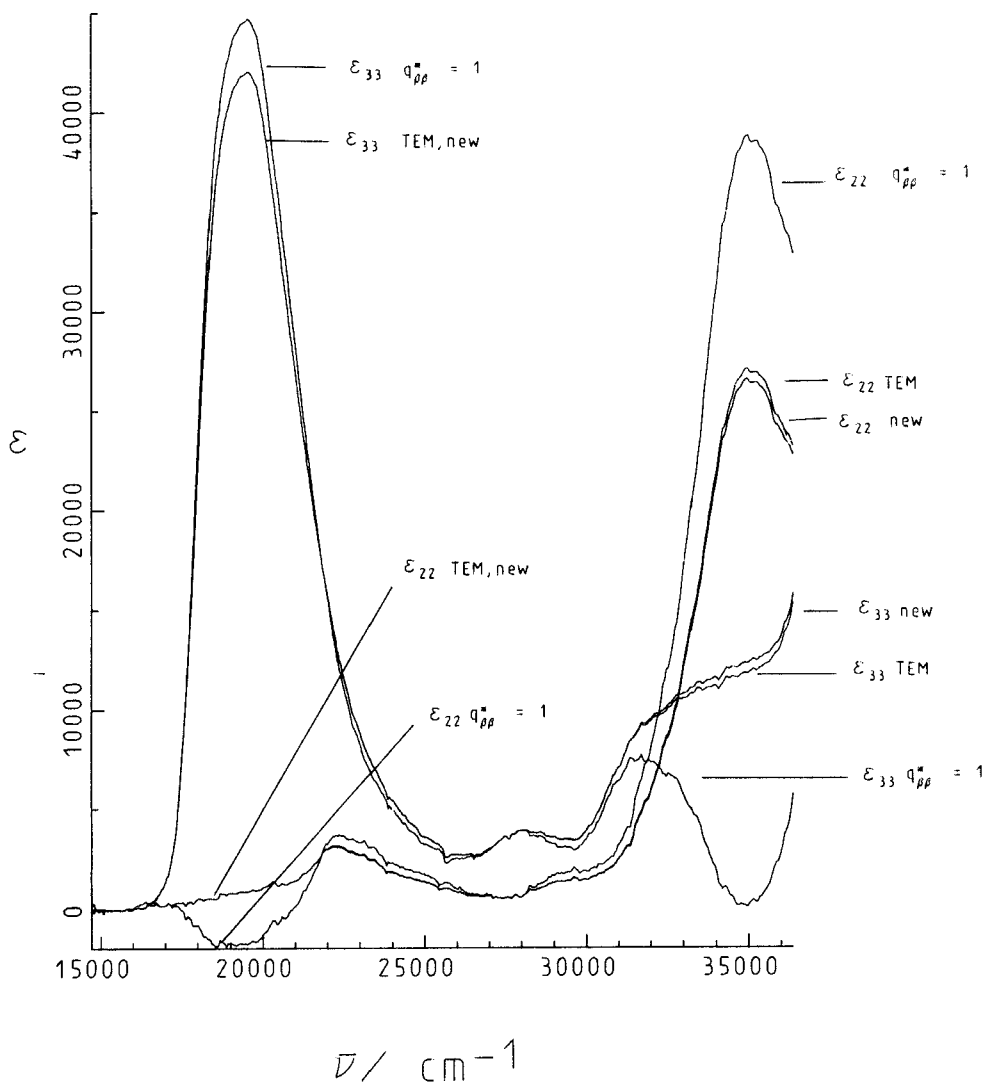
Figure 10. Reduced spectra of dye **6** calculated by different approximations.

Table 4. Values for amount of mixing in the $\bar{\nu}_2$ region ($q^*_{\beta\beta}(\bar{\nu}_2)$), the parameter $b/a$ and the order parameters $S^*$ and $D^*$ for the diaminoanthraquinones **1–7**.

| Dye | Symbol | Situation | $q^*_{\beta\beta}(\bar{\nu}_2)$ | $b/a$ | $S^*$ $(T = 311\,\mathrm{K})$ | $D^*$ |
|-----|--------|-----------|----------------|-------|-----------|-------|
| **1** | ◇ | 3$b$ | 0·95 | 0·57 | 0·63$_4$ | 0·07 |
| **2** | ☆ | 3$b$ | 0·84 | 0·78 | 0·34$_7$ | 0·14 |
| **3** | △ | 3$b$ | 0·87 | 0·41 | 0·52$_9$ | 0·07 |
| **4** | × | 2$b$ | 0·52 | 1·22 | 0·27$_0$ | 0·21 |
| **5** | + | 3$b$ | 0·92 | 0·62 | 0·51$_3$ | 0·10 |
| **6** |   | 3$b$ | 0·72 | 0·24 | 0·66$_5$ | 0·02 |
| **7** | ○ | 3$b$ | 0·68 | 0·37 | 0·32$_2$ | 0·06 |

regions, if the involved bands are polarized in the same plane. A function $R(\bar{v}_2, T) = \Phi(R(\bar{v}_1, T))$ can be derived which yields a straight line if $D^* = 0$ or in the trivial case where all bands concerned are polarized parallel to each other. The latter case can be discerned easily by the inspection of $R(\bar{v}, T)$, since the degree of anisotropy is then the same in both spectral regions. For $D^* = 0$, $S^*$ and the amount of overlap of the absorption bands in the region $\bar{v}_2$ can be determined from the slope of the straight line. By this the transition moment direction with respect to the $x_i^*$ system, i.e. $\beta$ in $q_{\beta\beta}^*(\bar{v}_2)$, cannot be fixed. However, the number of possible $\beta$ values is restricted by the area in which the experimental points appear. For $D^* \neq 0$ the position of the experimental points in different areas of the $R(\bar{v}_1)$, $R(\bar{v}_2)$ plane also allows the assignment of the transition moment direction with respect to the orientation axis. By means of the curvature of the resulting curve, the assignment is unequivocal if the measured points spread over a large range. It seems that this cannot always be easily realized experimentally because the temperature dependence of $R$ for liquid crystal guest–host systems, for example, is small, as is the temperature interval where the liquid crystal phase is stable.

There are six possibilities of placing the principal axes $x_i^*$ relative to the molecular framework portrayed here by the absorption behaviour, i.e. the transition moment tensor. Each area I–VIII in figure 2 can be assigned to some of the six spectroscopic situations given by the two transition moment directions with respect to the $x_i^*$ axes. Two situations have been realized experimentally. The diaminoanthraquiones 1–3 and 5–7 belong to the situation 3 *b* where the CT transition is polarized parallel to the orientation axis ($x_3^*$ axis) and the $x_2^*$ axis is parallel to the O=C $\cdots$ C=O direction. With dye 4 the orientation axis or the transition moment direction of the CT transition is switched with respect to the molecular framework compared with dyes 1–3 and 5–7. This means that the orientation axis or the CT transition moment is now parallel to the O=C $\cdots$ C=O direction. Because there is no reason for a change of the transition moment direction of the CT transition by the mesityl substituents in the 2 and 7 positions, we have to conclude a switch of the orientation axis. With dye 7, a molecule analogous to 4 in which the mesityl groups are replaced by phenyl groups, the orientation axis is parallel to the CT transition moment. It is astonishing that this drastic change can be accomplished by the six methyl groups which distinguish 4 from 7. There is no explanation for the exceptional behaviour of dye 4, but it seems to be really true that the methyl substitution is the essential point for this effect, because we found the same effect for non-symmetrically mesityl substituted diaminoanthraquinones. This will be discussed in a subsequent paper.

For the quantitative calculation of $S^*$ and $D^*$ the relation $D^* = f(S^*)$ between the order parameters as a function of temperature is required. It has been derived here from the contribution $\mathscr{S}$ of the orientational order to the entropy of the ordered system. The isentropics $\mathscr{S}(S^*, D^*) = $ constant have been calculated from an orienting potential with two independent parameters $a$ and $b$ which appear as variables of state. The curve $D^* = f(S^*, b/a)$ intersects the isentropics in points of constant slope $-a/b$, from which property it can easily be constructed. These curves are equal to those resulting from the mean field theory described by Luckhurst and co-workers [7]. Using this relation between $D^*$ and $S^*$ and the equations for the degree of anisotropy, the amount of overlap $q_{\beta\beta}^*(\bar{v}_2)$ as well as $b/a$ can be determined. The reduced spectra, i.e. the spectra decomposed into components belonging to different transition moment directions, as calculated from $q_{\beta\beta}^*(\bar{v}_2)$, are in agreement, within the margins of error of the method, with those from the T.E.M. model. This agreement is a good
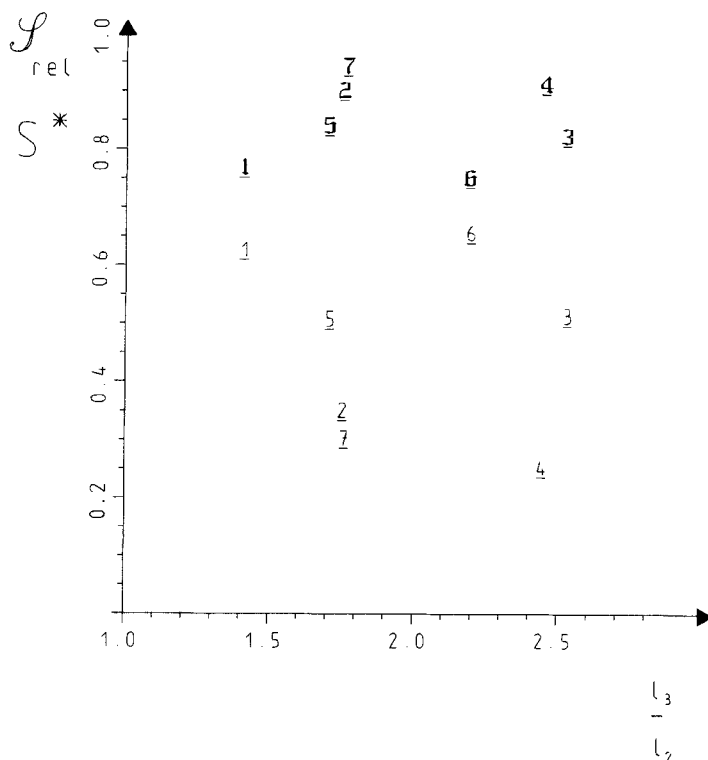
Figure 11. The order parameter $S^*$ and the entropy $\mathscr{S}$ versus the length-to-width ratio $l_3/l_2$ of the molecule ($T = 38°C$). For $\mathscr{S}$ the numbers of the compounds are written in English gothic.

justification for both methods, because they start from very different assumptions. Whereas T.E.M. assume certain spectroscopic features, with the method given here the use of our relation $D^* = f(S^*)$ is the essential point. Furthermore, the reduced spectra show that the neglect of a small overlap of bands leads to unacceptable results.

A structure–order parameter relation is often used in literature where $S^*$ is given as a function of the length to width ratio $l_3/l_2$ of the molecule. As can be seen from figure 11, such a relation does not hold for the diaminoanthraquinones analysed here. One may ask whether this deviation is an effect of the second order parameter $D^*$. This is not true, however, as can be seen from the respective values of $\mathscr{S}$ in figure 11. The relation between order parameters and the structure of diaminoanthraquinones will be discussed again in a subsequent paper, in the context of the investigation of a large number of symmetrically and non-symmetrically substituted compounds.

### References

[1] KUBALL, H.-G., ALTSCHUH, J., and SCHÖNHOFER, A., 1979, *Chem. Phys.*, **43**, 67.
[2] KUBALL, H.-G., STRAUSS, A., KAPPUS, M., FECHTER-RINK, E., SCHÖNHOFER, A., and SCHEROWSKY, G., 1987, *Ber. Bunsenges. phys. Chem.*, **91**, 1266.

[3] CLARK, M. G., and SAUNDERS, F. C., 1982, *Molec. Crystals liq. Crystals Lett.*, **82**, 267.
[4] KORTE, E. H., 1983, *Molec. Crystals liq. Crystals*, **100**, 127.
[5] THULSTRUP, E. W., and EGGERS, J. H., 1968, *Chem. Phys. Lett.*, **1**, 690. THULSTRUP, E. W.,
       MICHL, J., and EGGERS, J. H., 1970, *J. phys. Chem.*, **74**, 3868. MICHL, J., and THULSTRUP,
       E. W., 1986, *Spectroscopy with Polarized Light* (Verlag Chemie (VCH)).
[6] STRAUSS, A., and KUBALL, H.-G., 1987, Poster presentation ASI Meeting '*New Develop-
       ments in Polarized Optical Spectroscopy on Ordered Systems*', Rimini.
[7] HUMPHRIES, R. L., JAMES, P. G., and LUCKHURST, G. R., 1972, *J. chem. Soc. Faraday Trans.
       II*, **68**, 1031. LUCKHURST, G. R., ZANNONI, C., NORDIO, P. L., and SEGRE, U., 1975,
       *Molec. Phys.*, **30**, 1345. LUCKHURST, G. R., 1979, *The Molecular Physics of Liquid
       Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press), Chap. 4.
       EMSLEY, J. W., HASHIM, R., LUCKHURST, G. R., RUMBLES, G. N., and VIOLORIA, F. R.,
       1983, *Molec. Phys.*, **49**, 1321.