

## Circular Dichroism of Oriented Molecules. Electric dipole/magnetic dipole and electric dipole/electric quadrupole contribution for cholest-4-en-3-one

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Dedicated to the memory of Professor Dr. Günther Snatzke

**Abstract** : Three independent molecular quantities  $\Delta\epsilon_{ii}^*$  have been determined for 2,2,4,6,6-d<sub>5</sub>-cholest-4-en-3-one (**1**) by the circular dichroism of isotropic (CD) and anisotropic (ACD) samples using order parameters evaluated from <sup>2</sup>H NMR spectra. The orientation axis depends on temperature which may originate from a conformational change of **1**. A refined analysis of the ACD measurements is given and applied to **1** because all coordinates of the order tensor are known. The order of the molecules as calculated from <sup>2</sup>H NMR spectra is higher than that obtained by UV and IR spectroscopy. The estimated electric dipole/electric quadrupole contribution to the ACD is in the order of magnitude of the electric dipole/magnetic dipole contribution.

### 1. Introduction

The circular dichroism ( $\Delta\epsilon$ ) measurements in the visible and UV spectral region have been used in the last three decades as an outstanding tool to determine the absolute configuration and/or conformations of molecules in solution. With this method, the "chromophores" contained in a molecule are used as "markers" of their own chirality (inherently dissymmetric chromophores) or the chirality of their surroundings (inherently symmetric chromophores). Rules are then required which correlate the sign of the Cotton effect (CE) of the chromophore to the absolute configuration of the molecule or, more specifically, of the chromophore and its surroundings. In general, this correlation can be obtained by a numerical quantum mechanical calculation or be expressed by chirality functions<sup>1</sup> or, in the most frequently applied form, by empirical sector or helicity rules<sup>2</sup>. Many rules which can be applied to various classes of molecules<sup>2</sup> have been derived empirically for different types of transitions in different chromophores. Breakdowns sometimes occur. Therefore, there is a need to

find the limitations of such rules in order to have a secure field of application. The knowledge of the CD of oriented molecules allows to determine  $\Delta\varepsilon$  as a sum of three independent quantities  $\Delta\varepsilon_{ii}$ :

$$\Delta\varepsilon = \frac{1}{3}(\Delta\varepsilon_{11} + \Delta\varepsilon_{22} + \Delta\varepsilon_{33}). \quad (1)$$

The  $\Delta\varepsilon_{ii}$  are new possible pieces of information. They may help to analyze the failure of helicity rules<sup>3</sup> since in going from one enantiomer or local enantiomer to the other not only  $\Delta\varepsilon$  but also each  $\Delta\varepsilon_{ii}$  has to change its sign.

Furthermore,  $\Delta\varepsilon_{ii}$  can be separated into two parts:  $\Delta\varepsilon_{ii}^{\mu m}$  and  $\Delta\varepsilon_{ii}^{\mu Q}$ , the electric dipole/magnetic dipole and the electric dipole/electric quadrupole contribution. Nowadays, sector and helicity rules are given for  $\sum_i \varepsilon_{ii}^{\mu m} = 3\Delta\varepsilon$  whereas the other pieces of chirality information  $\Delta\varepsilon_{ii}^{\mu Q}$  ( $i = 1, 2, 3$ ) are only measurable in an anisotropic medium. They cancel in an isotropic solution. The knowledge of the  $\Delta\varepsilon_{ii}^{\mu Q}$  may open a new field to receive structural information by new sector rules for this electric dipole/electric quadrupole contribution. The  $\Delta\varepsilon_{ii}$  and thus the  $\Delta\varepsilon_{ii}^{\mu Q}$  can be evaluated from CD measurements of anisotropic samples ( $\Delta\varepsilon^A$ ) which can now be done with fair accuracy because a better experimental technique and a developed theoretical description are available<sup>3</sup>. There are two problems with the determination of  $\Delta\varepsilon^A$ :

- the artifactfree measurement of  $\Delta\varepsilon^A$ , i.e. the avoidance of linear dichroism and birefringence,
- the determination of the amount of orientation for molecules of low symmetry.

In this paper a refined analysis of the ACD will be described for a molecule of low symmetry, cholest-4-en-3-one (1), the order tensor of which is now available by <sup>2</sup>H NMR spectroscopy. Furthermore, an estimate of the orientation of the relevant coordinate systems, i.e. the principal axes of the order tensor  $g_{ij33}$  (orientational distribution tensor), the tensor of rotation, and the transition moment tensor will be given.

## 2. Experimental

2,2,4,6,6-d<sub>5</sub>-cholest-4-en-3-one (1) was prepared from the parent enone by base-catalyzed deuteration by the procedure of Shapiro *et al.*<sup>4</sup>. The crude product was purified by column chromatography on Kieselgel 60 (70-230 mesh, Merck) and crystallized from deuteromethanol. To measure the ACD, the UV, and the polarized UV spectra of 1 (there is no influence of deuteration on these effects), the compound was dissolved (about 3% in weight) in the nematic phase of ZLI 1695 (Merck, mixture of four 4-n-alkyl-4-cyanobicyclohexanes). The sample was filled into a special cuvette<sup>5</sup> where the chiral induction is compensated by an electric ac field (10<sup>6</sup> V/m) and then adjusted in a commercial CD spectrometer (Jobin Yvon Mark IV). For the ACD measurements the optical axis of the nematic uniaxial phase was chosen to be parallel to the propagation direction of the light beam. In order to ensure that the results are not falsified by linear birefringence and dichroism artifacts, various  $\Delta\varepsilon^A$  measurements were done with the sample being rotated about the propagation direction of the light beam into six positions differing by 30°. If there is no or only a small influence of the rotations on  $\Delta\varepsilon^A$ , the mean value can be used to evaluate further data. In order to check for a possible decomposition at first  $\Delta\varepsilon$  ( $T = 80$

°C), then  $\Delta\epsilon^A$  (six times for each temperature), and then again  $\Delta\epsilon$  ( $T = 80$  °C) were measured. The degree of anisotropy  $R$  was determined by polarized spectroscopy with the UV spectrometer Varian Cary 2200<sup>6</sup>. The <sup>2</sup>H NMR spectra were obtained on a Bruker AMX 400 spectrometer. Because  $\Delta\chi$  is negative for ZLI 1695, the phase is cholesteric with the NMR measurements (chiral induction). For comparison, the order parameters of **1** were also determined in ZLI 1132 (Merck, mixture of phenylcyclohexanes and biphenylcyclohexanes) where the phase is nematic for a magnetic induction  $B = 9.4$  T ( $\Delta\chi > 0$ ), and in a compensated cholesteric phase composed of cholesteryl chloride (CC) and cholesteryl laurate (CL) (1.8:1 and 1.6:1 per weight,  $\Delta\chi < 0$ ). To control the temperature of the probes for the different measurements (ACD, NMR, etc.), the temperature units were calibrated with a Pt 100 resistor.

### 3. Working equations and evaluation of data

As from <sup>2</sup>H NMR spectroscopy the order tensor is, in principle, available, the evaluation of the ACD and polarized absorption data can be done in a more exact way than before<sup>3,7</sup>. This means that for the ACD of molecules of low symmetry where the orientation of the principal axes of the order tensor  $g_{ij33}$  (see appendix) relative to the molecular frame is temperature-dependent, we may now use the formula

$$\Delta\epsilon^A = \sum_{i,j} g_{ij33} \Delta\epsilon_{ij} = \sum_{i,j} a_{ij}^2 g_{ij33}^* \Delta\epsilon_{ii}^{\circ} \quad (2)$$

The  $\Delta\epsilon_{ij}$  and  $g_{ij33}$  ( $i, j = 1, 2, 3$ ) refer to an arbitrary molecule-fixed  $x_i$  coordinate system. For convenience, that coordinate system will be chosen in which the geometry of the molecule known from X-ray analysis<sup>8</sup> has been given. The eigenvalues  $g_{ii33}^*$  describe the order in the system of principal axes ( $x_i^*$ ) of  $g_{ij33}$  whereas the eigenvalues  $\Delta\epsilon_{ii}^{\circ}$  give the molecular property  $\Delta\epsilon_{ij}$  in its system of principal axes ( $x_i^{\circ}$ ).  $a_{ij}$  are the elements of the matrix which transforms the  $x_i^*$  into the  $x_i^{\circ}$ . One can imagine the molecular quantities  $\Delta\epsilon_{ii}^{\circ}$  as the result of a CD measurement with light propagating along the molecular  $x_i^{\circ}$  axis. The  $\Delta\epsilon_{ij}$  can be decomposed into an electric dipole/magnetic dipole and an electric dipole/electric quadrupole contribution,

$$\Delta\epsilon_{ij}(\bar{\nu}) = \Delta\epsilon_{ij}^{\mu m}(\bar{\nu}) + \Delta\epsilon_{ij}^{\mu Q}(\bar{\nu}) \quad (3)$$

In order to get rid of the frequency dependence one can calculate the anisotropic rotational strength  $R^A$  for the electronic transition  $N \rightarrow K^7$

$$R^A = \frac{3}{B} \int \frac{\Delta\epsilon^A(\bar{\nu})}{\bar{\nu}} d\bar{\nu} = 3 \sum_{i,j} g_{ij33} R_{ij}^{NK}; \quad \frac{3}{B} = 22.96 \cdot 10^{-40} \text{ (cgs)} \quad (4)$$

For an isotropic solution,  $g_{ij33} = \frac{1}{3} \delta_{ij}$ , and  $R^A$  becomes the rotational strength  $R^{NK} = \sum_i R_{ii}^{NK}$ ;  $R_{ij}^{NK}$  is the tensor of rotation:

$$R_{ij}^{NK} = \frac{1}{B} \int \frac{\Delta \epsilon_{ij}(\bar{\nu})}{\bar{\nu}} d\bar{\nu}. \quad (5)$$

The decomposition of  $R_{ii}^{NK}$  corresponding to the decomposition in eq. (3) yields

$$R_{11}^{\mu m} = \text{Im} \left\{ \langle \mu_2 \rangle_{NK} \langle m_2 \rangle_{KN} + \langle \mu_3 \rangle_{NK} \langle m_3 \rangle_{KN} \right\}, \quad (6)$$

$$R_{11}^{\mu Q} = -\langle \mu_2 \rangle_{NK} \langle Q_{31} \rangle_{KN} + \langle \mu_3 \rangle_{NK} \langle Q_{21} \rangle_{KN}. \quad (7)$$

The other coordinates  $R_{ii}^{NK}$  ( $i = 2, 3$ ) are received by cyclic permutation of the indices.  $\langle \mu_i \rangle_{NK}$ ,  $\langle m_i \rangle_{KN}$ , and  $\langle Q_{ij} \rangle_{KN}$  are the electric dipole, magnetic dipole, and electric quadrupole transition moments.

The molar decadic absorption coefficient for light polarized parallel ( $\epsilon_1$ ) and perpendicular ( $\epsilon_2$ ) to the optical axis of a uniaxial sample is given by

$$\epsilon_k = \sum_{i,j} g_{ijkk} \epsilon_{ij} = \sum_{i,j} a_{ij}^2 g_{jjkk}^* \epsilon_{ii}^+ \quad (k = 1, 2). \quad (8)$$

$\epsilon_{ii}^+$  are the absorption coefficients for a light beam polarized linearly parallel to  $x_i^+$  (principal axes of  $\epsilon_{ij}$ ) in a completely oriented system. They are connected to the absorption coefficient of the isotropic solution by

$$\epsilon = \frac{1}{3}(\epsilon_1 + 2\epsilon_2) = \frac{1}{3}(\epsilon_{11}^+ + \epsilon_{22}^+ + \epsilon_{33}^+). \quad (9)$$

Furthermore, from eq. (8) follows for the degree of anisotropy

$$R = \frac{1}{2} \sum_{i,j} (3g_{ij33} - \delta_{ij}) q_{ij}; \quad q_{ij} = \frac{\epsilon_{ij}}{3\epsilon}. \quad (10)$$

If the molecule-fixed coordinate system is arbitrarily chosen, non-diagonal elements should be taken into account in eq. (10).

This refinement of the description of the ACD and the polarized UV absorption in comparison with our earlier papers is appropriate because the nuclear quadrupole coupling in the  $^2\text{H}$  NMR spectra allows the determination of all elements of the order tensor  $g_{ij33}$  for 1. Here we have to use the assumption that only one conformation exists, i.e. that the molecule is rigid. From equations given by Veracini<sup>9</sup>, for the splitting of the  $^2\text{H}$  NMR signal of one C-D bond there follows, written in our notation, for a host system with  $\Delta\chi < 0$

$$\Delta\nu = -\frac{3}{4} \sum_{i,j} g_{ij33} \xi_{ij}. \quad (11)$$

$\xi_{ij}$  is the nuclear quadrupole tensor. To determine all elements  $g_{ij33}$ , the signals of five different C-D bonds within the molecules are necessary where not more than two bond directions lie in the same plane. For the evaluation their splittings  $\Delta\nu$  are measured as functions of temperature. The diagonal and rotationally symmetric nuclear quadrupole tensors  $\xi'_{ij}$  which refer to the five bond directions ( $\xi'_{33} = 185$  kHz for a  $sp^2$ - and 170 kHz for a  $sp^3$ -bond;  $\eta = 0$ )<sup>9</sup> are transformed to the  $x_i$  coordinate system. With the resulting five tensors  $\xi_{ij}$  eq. (11) yields a system of five linear equations from which all independent coordinates  $g_{ij33}$  can be obtained. By diagonalization of the order tensor there follow then the order parameters  $S^*$ ,  $D^*$ , and the orientation of the principal axes of the order tensor with respect to the originally chosen molecule-fixed  $x_i$  coordinate system. In the case of sufficient accuracy of the measurements of the polarized UV absorption and the ACD spectra the principal axes of the tensors  $\varepsilon_{ij}$  and  $\Delta\varepsilon_{ij}$  can be estimated.

The analysis of  $\Delta\varepsilon^A$ ,  $\Delta\varepsilon$ ,  $R$ , and the NMR spectra as functions of temperature will be demonstrated subsequently. One of the problems is that the coordinates of the order tensor of **1** were determined for the cholesteric state of ZLI 1695. They have to be assumed to be equal to those of the guest **1** in the nematic phase of ZLI 1695 in which  $\Delta\varepsilon^A$  and  $R$  were measured.

## 4. Results

### 4.1. Order parameters

Fig. 1 shows the  $^2H$  NMR spectrum of **1** in ZLI 1695 at  $T = 29$  °C. From the clear splittings of the signals of the five C-D bonds we get five independent pieces of information which can be used to evaluate the order tensor  $g_{ij33}$  from a set of linear equations derived from eq. (11). The assignment of the splittings to the different C-D bonds of **1** results from the approximate calculation of  $\Delta\nu$  by assuming an orientation axis and an approximate order known from UV measurements of this and similar compounds<sup>3</sup>

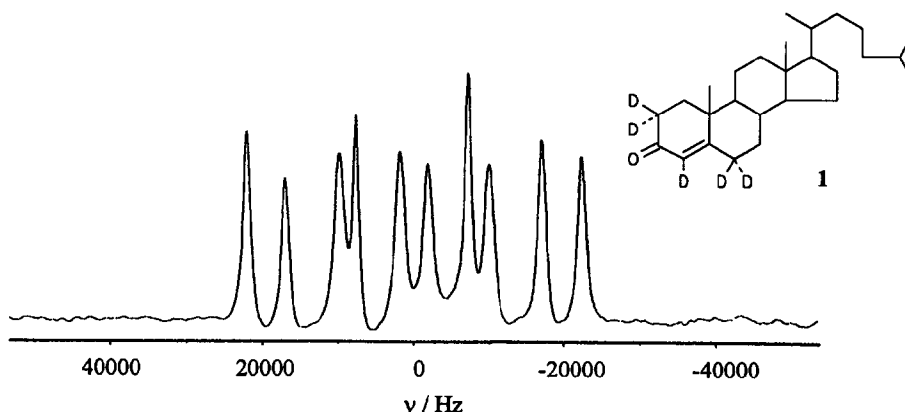


Fig. 1.  $^2H$  NMR spectrum of **1** in ZLI 1695 at  $T = 29$  °C; assignment of the quadrupole splittings  $\Delta\nu$  of the five deuterons at positions  $6\alpha$ ,  $4$ ,  $2\alpha$ ,  $6\beta$ ,  $2\beta$ : -15.0553, 3.7028, 19.8568, 34.1797, 44.4743 kHz.

The order parameters  $S^*$ ,  $D^*$  and their temperature dependence are given in fig. 2. Whereas  $D^*$  is nearly temperature-independent,  $S^*$  shows a variation as expected for such types of molecules. The orientation of the principal axes of  $g_{ij33}$  is also temperature-dependent. This means that the order parameters refer to axes which vary within the molecule with temperature. For  $T = 29^\circ\text{C}$  the orientation of the principal axes of  $g_{ij33}$  with respect to the skeleton of **1** is given in fig. 3a. The orientation of the  $-\text{C}_8\text{H}_{17}$  chain in 17-position given in fig. 3a results from the X-ray analysis<sup>8</sup>. From the opinion that the orientation of a molecule in a nematic phase is determined by the length-to-breadth ratio one may expect in the liquid crystal guest/host system a chain which is not so far apart from the  $x_3^*$  axis as in the crystalline state shown in fig. 3a. Thus, the temperature dependence of the orientation of the  $x_i^*$  axes with respect to the molecular skeleton which only amounts to few degrees (fig. 3b) may result from the change of conformations of the  $-\text{C}_8\text{H}_{17}$  chain. The chain is expected to wind around the  $x_3^*$  axis and, therefore, is essential for the direction of this axis relative to the skeleton. Because in ZLI 1695 the measurements were done in an induced cholesteric phase, the order parameters of **1** in a nematic phase ZLI 1132 and a compensated cholesteric phase are given for comparison in fig. 2. They are about 10% smaller for **1** in CC/CL; this agrees with results from UV and IR measurements. The  $x_i^*$  axes are temperature-dependent in these solvents, too.

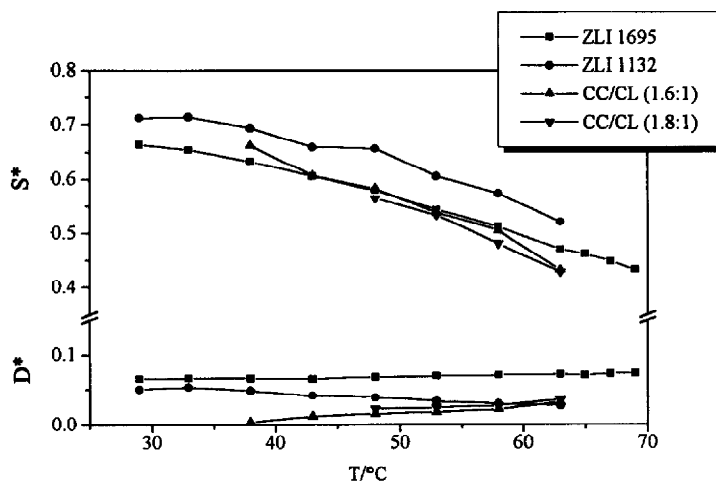


Fig. 2. Temperature dependence of the order parameters  $S^*$ ,  $D^*$  in ZLI 1695, ZLI 1132 and CC/CL. The orientation of the principal axes belonging to these order parameters is temperature-dependent.

$$S^* = (3g_{3333}^* - 1)/2; D^* = \sqrt{3}(g_{2233}^* - g_{1133}^*)/2.$$

#### 4.2. Polarized spectroscopy

$\Delta\epsilon^A$  shows a very strong temperature dependence in ZLI 1695 (fig. 4a). The variation with respect to  $\Delta\epsilon$  is large as shown in fig. 4b by  $\Delta\epsilon^A - \Delta\epsilon$ . The degree of anisotropy  $R$  (fig. 5) is small as known from earlier measurements<sup>3</sup>. The tensor coordinates  $\Delta\epsilon_{ij}$  and  $\epsilon_{ij}$  can be calculated by assuming the transferability of the order parameters from the experimental situation of a NMR experiment to those of ACD and polarized UV

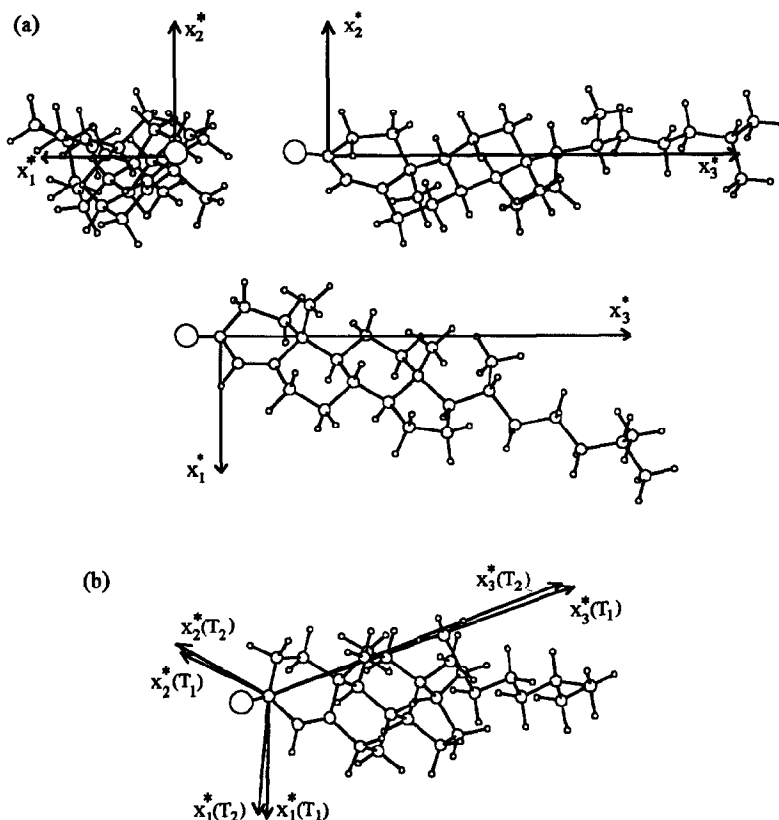


Fig. 3. (a) Principal axes ( $x_i^*$ ) of the order tensor of 1 in ZLI 1695 at  $T = 29^\circ\text{C}$  with respect to the molecular skeleton derived from X-ray analysis.

(b) Comparison of the principal axes of 1 in ZLI 1695 at  $T = 29^\circ\text{C}$  ( $x_i^*(T_1)$ ) and  $T = 63^\circ\text{C}$  ( $x_i^*(T_2)$ ).

measurements. Only with a temperature-dependent orientation of the principal  $x_i^*$  axes of  $g_{ij33}$  sufficient information is available to calculate  $\Delta\epsilon_{ij}^*$  and  $\epsilon_{ij}^*$  and the corresponding principal axes. The change of the orientation of the  $x_i^*$  axes is small as shown in fig. 3b. For this reason, we were only able to calculate the diagonal elements  $\Delta\epsilon_{ii}^*$  and from these the quantities  $\Delta_1^*$  defined by

$$\Delta_1^* = \frac{1}{2}(\Delta\epsilon_{11}^* - \Delta\epsilon_{22}^* - \Delta\epsilon_{33}^*) \quad (12)$$

and cyclic permutation of the indices 1, 2, 3. The  $\Delta_i^*$  yield information about the electric dipole, magnetic dipole, and electric quadrupole transition moments for a transition between two different vibronic-electronic states  $|0\rangle \rightarrow |n\rangle$  with the spectral function  $G^{0n}(\nu)$ :

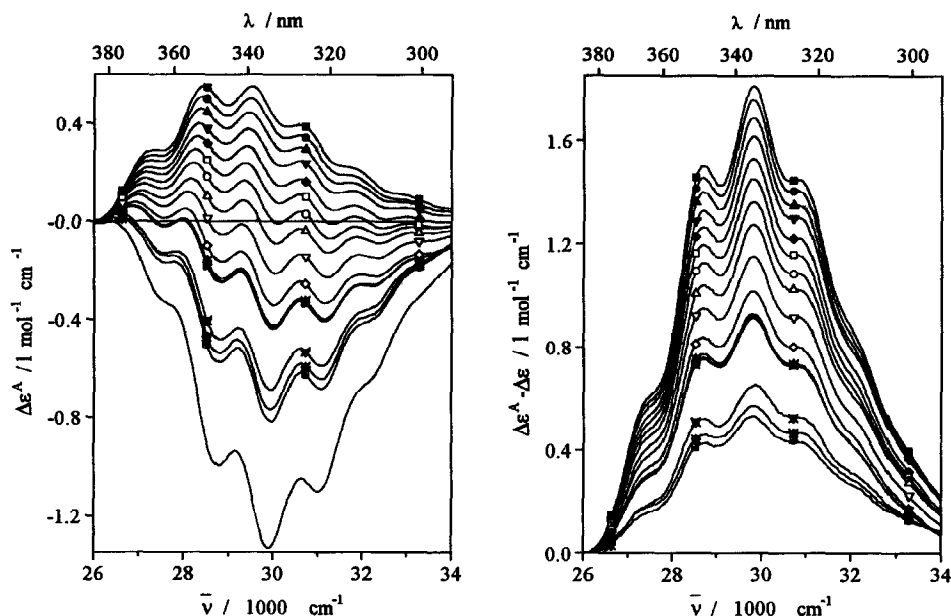


Fig. 4. Temperature dependence of  $\Delta\epsilon^A$  and  $\Delta\epsilon$  (—) (left) and of  $\Delta\epsilon^A - \Delta\epsilon$  (right) for the  $\pi\pi^*$  transition of **1** in ZLI 1695.

$T / ^\circ\text{C}$ : ■ /29.0; ● /33.0; ▲ /38.0; ▼ /43.2; ◆ /48.0; □ /52.1; ○ /55.8; △ /59.0; ▽ /61.8;  
 ◇ /64.4; ☒ /65.0; ☓ /65.7; ✕ /66.4; ✖ /66.8; ✗ /67.0; ☐ /67.2

$$\Delta_i(\bar{\nu}) = -\frac{1}{2} B \bar{\nu} \sum_n \text{Im} \{ \langle \mu_i \rangle_{\text{on}} \langle m_i \rangle_{\text{no}} \} G^{\text{on}}(\bar{\nu}) + \Delta \epsilon_{ii}^{\mu\text{Q}}(\bar{\nu}) \quad (13)$$

The  $\Delta_i^*$  for **1** are given in fig. 7. The corresponding quantities for the rotation tensor can be obtained by applying eq. (5) to the  $\Delta_i$ .

## 5. Discussion

### 5.1. Polarized absorption

The order parameter  $S^*$  determined by polarized spectroscopy at  $T = 38^\circ\text{C}$  is 0.35 in CC/CL. In ZLI 1695 at  $T = 38^\circ\text{C}$   $S^* = 0.63$  was found from  $^2\text{H}$  NMR spectroscopy. The difference of these two values is larger than expected from the influence of the different host properties. Correcting  $S$  for the solvent effect there is an unaccountable amount of about 20%. Because of the neglect of  $D^*$  for the polarized UV spectra the calculated  $S$  values do not refer to the orientation axis ( $x_3^*$ ). But using another axis than  $x_3^*$  leads to an order parameter  $S < S^*$  as has been shown before<sup>10</sup>. Furthermore, the amount of mixing of the contributions with



different polarizations (vibrational coupling) may have been overestimated in the earlier paper<sup>3</sup>. If the temperature dependence of the orientation axis is neglected, the  $\epsilon_{ii}^*$  values given in fig. 5 can also be calculated from

$$\epsilon_1 - \epsilon = (\epsilon_{33}^* - \epsilon)S^* + \frac{1}{\sqrt{3}}(\epsilon_{22}^* - \epsilon_{11}^*)D^* \quad (14)$$

which follows from eq. (8).  $\epsilon_{33}^* > \epsilon_{11}^* + \epsilon_{22}^*$  as found in reference <sup>3</sup> is confirmed here. The "forbidden" progression which determines the intensity of  $\epsilon_{33}^*$  contributes about 60% to the total absorption.  $\epsilon_{11}^*$  is of the same order of magnitude as  $\epsilon_{22}^*$  but the experimental error is very large as shown by the error bars in fig. 5. From the band structure of  $\epsilon_{22}^*$  one may conclude that  $\epsilon_{22}^*$  is determined by the "allowed" progression. Both vibrational progressions ("allowed" and "forbidden") are indicated by weakly marked small maxima shifted against each other about  $\Delta\bar{\nu} = 700 - 1000 \text{ cm}^{-1}$ . Accepting this conclusion, the polarization of the "allowed progression" is directed from the C=O to the C=C bond ( $\parallel x_2$ , fig. 6); this results from the interaction of both groups which include a dihedral angle about the C(3)-C(4) bond of a few degrees.

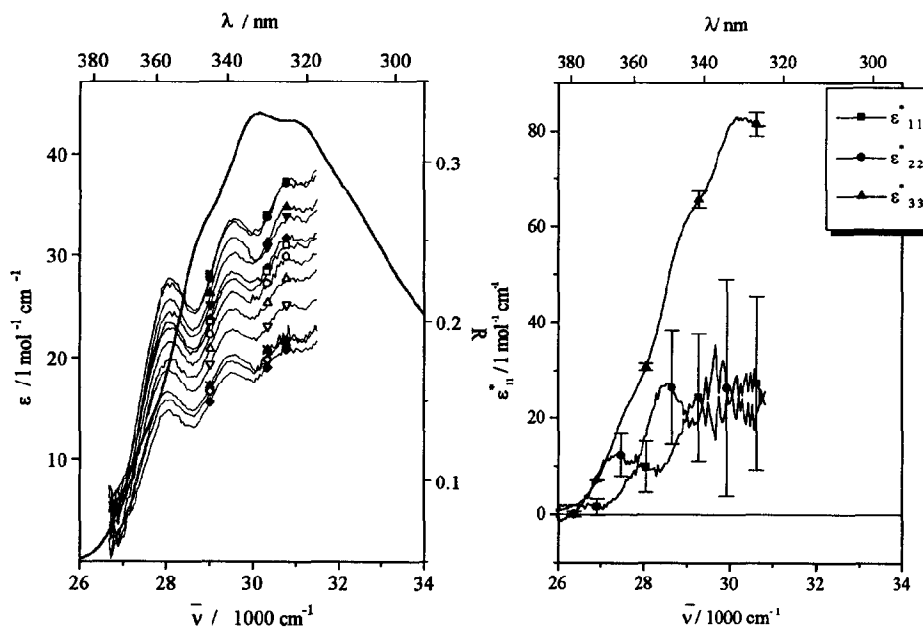


Fig. 5. Temperature dependence of the degree of anisotropy  $R$  for the  $n\pi^*$  transition and the molar decadic absorption coefficient  $\epsilon$  (—) of **1** in ZLI 1695 at  $T = 80^\circ\text{C}$  (left); reduced absorption coefficients  $\epsilon_{ii}^*$  of the  $n\pi^*$  transition of **1** (right).  
 $T/^\circ\text{C}$ :  $\blacksquare$  /29.0;  $\bullet$  /33.0;  $\blacktriangle$  /38.0;  $\blacktriangledown$  /43.2;  $\blacklozenge$  /48.0,  $\square$  /52.1;  $\circ$  /55.8;  $\triangle$  /59.0,  $\triangledown$  /61.8,  $\diamond$  /64.4;  $\otimes$  /66.4;  $\diamond$  /67.2

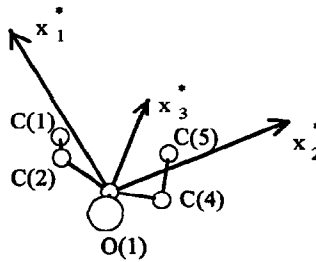


Fig. 6. The principal axes of the order tensor with respect to the 4-en-3-one chromophore; the  $x_2^*$  axis includes an angle of 45-55° with the C(2)-C(3)-C(4) plane.

## 5.2. Anisotropic circular dichroism (ACD)

If the temperature dependence of the orientation axis is neglected, the  $\Delta\epsilon_{ii}^*$  values given in fig. 7 can also be calculated from

$$\Delta\epsilon^A - \Delta\epsilon = (\Delta\epsilon_{33}^* - \Delta\epsilon_{11}^*)D^* + \frac{1}{\sqrt{3}}(\Delta\epsilon_{22}^* - \Delta\epsilon_{11}^*)D^* \quad (15)$$

which follows from eq. (2). The  $\Delta\epsilon_{ii}^*$  refer to the principal axes of the order tensor.  $\Delta\epsilon_{33}^* > 0$  and  $\Delta\epsilon_{11}^* + \Delta\epsilon_{22}^* < 0$  is confirmed within the experimental error given by the bars in fig. 7<sup>3</sup>. From the analysis of  $\Delta\epsilon^A(T)$  it can be concluded that the  $x_i^*$  system differs from the  $x_i^\circ$  system. The orientation of both coordinate systems relative to each other cannot be obtained because of insufficient accuracy of the experimental data.

$\Delta\epsilon_{33}^*$  gains its intensity by the "allowed" progression<sup>3</sup> (allowed with respect to an assumed planar en-one chromophore) polarized parallel to the  $x_2^*$  axis. The  $x_2^*$  axis includes an angle of 45-55° with the C(2)-C(3)-C(4) plane (fig. 6; in the earlier paper<sup>3</sup> the  $x_1^*$  axis was assumed to be perpendicular to the en-one plane). Determination of the order tensor and  $\Delta\epsilon^A$  with very high accuracy near the phase transition are necessary which are difficult to perform. Furthermore, a good evaluation of the nondiagonal elements is only possible if the temperature dependence of the orientation of the  $x_i^*$  axes is sufficiently large.  $\Delta\epsilon_{22}^*$  is determined by the "forbidden" progression polarized along the orientation axis. For the evaluation of the  $\Delta\epsilon_{ii}^{\mu Q}$ , linear combinations of the  $\Delta\epsilon_{ii}$  ( $i = 1, 2, 3$ ) yield a decomposition according to eq. (13) if the electric dipole transition is polarized perpendicular to an  $x_i^*$  axes. The  $n\pi^*$  transition is an allowed magnetic dipole transition polarized parallel to the C=O bond direction, i.e.  $\langle m_3 \rangle_{KN} \neq 0$ . Together with the result  $\epsilon_{11}^*, \epsilon_{22}^* < \epsilon_{33}^*$ , the conclusion that  $\langle \mu_3 \rangle_{NK} \langle m_3 \rangle_{KN}$  is the main contribution to  $\Delta\epsilon$  is further supported. With these assumptions the electric dipole/magnetic dipole contribution can be estimated from eq. (13) to be  $\Delta\epsilon_{11}^{\mu Q} \cong \Delta_1^*$ ,  $\Delta\epsilon_{22}^{\mu Q} \cong \Delta_2^*$ , and  $\Delta\epsilon_{33}^{\mu Q} \cong \Delta_3^* + 3/2 \Delta\epsilon = (\Delta_1^* + \Delta_2^*)$ . The decomposition eq. (13) is origin-dependent (the position of the origin used for the calculation here is the C(2) atom).

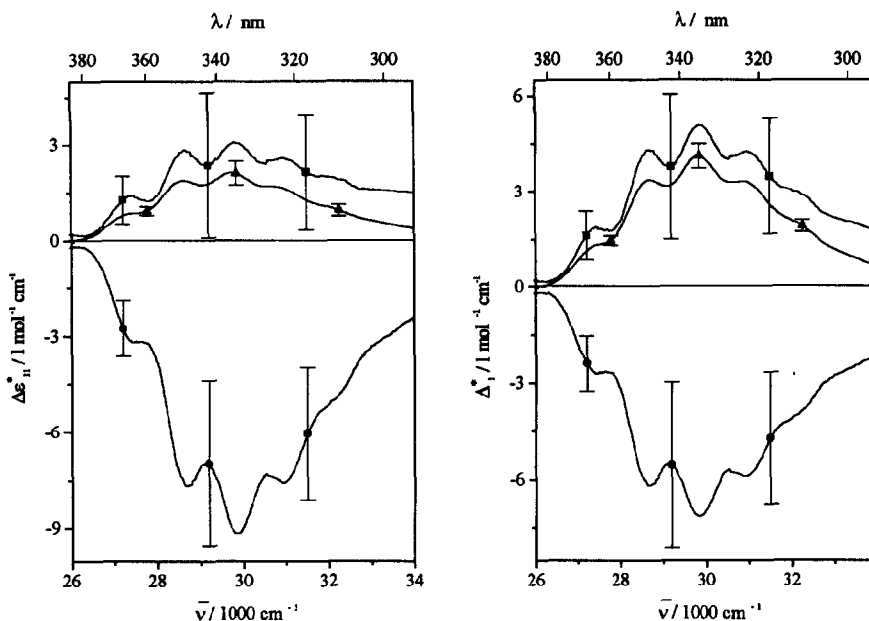


Fig. 7.  $\Delta \epsilon_{ii}^*$  of the  $n\pi^*$  transition of 1. Integration of  $\Delta \epsilon_{ii}^*$  according to eq. (5) yields  $R_{11}^{NK} = 4 \pm 2 \cdot 10^{-40}$ ,  $R_{22}^{NK} = -10 \pm 2 \cdot 10^{-40}$ ,  $R_{33}^{NK} = 2 \pm 0.2 \cdot 10^{-40}$  (cgs);  $\Delta_i^*$  ( $\nabla$ ) for the  $n\pi^*$  transition of 1. Integration according to eq. (5) yields  $\Delta_1^* = 6 \pm 2.8 \cdot 10^{-40}$ ,  $\Delta_2^* = -8 \pm 2.8 \cdot 10^{-40}$ ,  $\Delta_3^* = 4 \pm 2.8 \cdot 10^{-40}$  (cgs).  
 $\Delta \epsilon_{11}^*$  ( $\blacksquare$ );  $\Delta \epsilon_{22}^*$  ( $\bullet$ );  $\Delta \epsilon_{33}^*$  ( $\blacktriangle$ )  $\Delta_1^*$  ( $\blacksquare$ );  $\Delta_2^*$  ( $\bullet$ );  $\Delta_3^*$  ( $\blacktriangle$ )

The tensor coordinates  $\Delta \epsilon_{ii}^{\circ}$  yield information by means of light beams propagating along three mutually perpendicular directions through the molecule. From them the  $\Delta \epsilon_{ii}^{\mu Q}$  are available if one or two of the electric transition moment coordinates are equal to zero. From the spectroscopic point of view it is interesting to see that the electric dipole transition moment as well as the electric quadrupole transition moment can be calculated. From the stereochemical point of view there are not sufficient data available to establish from the new chirality information  $\Delta \epsilon_{ii}$ ,  $\Delta_i$ , and sometimes  $\Delta \epsilon_{ii}^{\mu Q}$  rules connecting their signs with structural properties of the molecules. It should be emphasized that these data can be obtained using CD, ACD, UV, and polarized UV spectra in combination with, e.g.  $^2\text{H}$  NMR measurements. Now there is a situation comparable to that time when Günther Sznatzke started his successful work in finding correlations between structural properties and the sign and magnitude of  $\Delta \epsilon$ . In the same way new information from the  $\Delta \epsilon_{ii}$  or  $R_{ii}^{NK}$  may be expected in future.

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### Appendix

Nonspherical molecules are anisotropic, i.e. from any point of reference they exhibit different properties in different spatial directions. Physical properties of such molecules cannot be described by scalar quantities alone, but vectors and tensors are also needed. For the refined analysis of our data it is impossible to dispense with the use of tensor properties. Three tensors are of exceptional importance for our discussion: the transition moment or the absorption tensor ( $D_{ij}^{NK}$  or  $\epsilon_{ij}$ )<sup>3</sup>, the rotation or the circular dichroism tensor ( $R_{ij}^{NK}$  or  $\Delta\epsilon_{ij}$ )<sup>3</sup>, and the order tensor ( $g_{ij33}$ ). For each tensor there exists a coordinate system with distinct significance, the system of principal axes. Here only the diagonal elements of the tensor are different from zero. For molecules without any symmetry the principal axes of the three tensors do not coincide and they are all needed to describe the spectroscopy:  $x_1^+$  for  $D_{ij}^{NK}$  or  $\epsilon_{ij}$ ,  $x_1^o$  for  $R_{ij}^{NK}$  or  $\Delta\epsilon_{ij}$ , and  $x_1^*$  for  $g_{ij33}$ . The  $x_3^*$  axis is called the "orientation axis".

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