47. Optical Activity of Oriented Molecules
IV. The Anisotropic CD. and UV. Spectra of Testosterone Propionate

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Dedicated to the memory of *Heinrich Labhart*

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Summary

Starting from the circular dichroism (CD.) of testosterone propionate oriented in a liquid crystal matrix it is shown that the CD., measured with light beams having different directions of propagation with respect to the molecular framework, is different in magnitude and frequency dependence. The vibrational structure is analysed.

From the concentration and temperature dependence of the CD. and UV. spectra an order parameter p and its concentration and temperature dependence is derived. By this an estimation for the direction of the transition moment of the $n \to \pi^*$ transition is given.

1. Introduction. – 1.1. *The circular dichroism (CD.) spectra.* The CD. of an aniso-tropic system can be given by

$$\Delta\varepsilon^A(\tilde{\nu}) = B\,\tilde{\nu}\,g_{ij33} \sum_n \sum_{Kk} R_{ij}^{NnKk}\, G^{NnKk}(\tilde{\nu}) \tag{1 a)[1]}$$

$$B = \frac{32\,\pi^3 N_L}{10^3\,hc\ln 10} \tag{1 b}$$

$$R_{ij}^{NnKk} = \frac{1}{4}\langle\mu_r\rangle_{NnKk}\{\varepsilon_{rsj}\langle C_{si}\rangle_{KkNn} + \varepsilon_{rsi}\langle C_{sj}\rangle_{KkNn}\} \tag{2 a}$$

$$\langle C_{si}\rangle_{KkNn} = -i\varepsilon_{sir}\langle m_r\rangle_{KkNn} - \frac{\omega_{KkNn}}{2c}\langle Q_{si}\rangle_{KkNn}. \tag{2 b}$$

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[1]   The index notation of vectors and tensors is used: μ_i is a vector coordinate, D_{ij} a tensor coordinate. Repeated tensor indices indicate a summation over 1, 2 and 3.

R_{ij}^{NnKk} is the tensor of rotation and $G^{NnKk}(\tilde{v})$ the spectral function of the CD. for the transition $|Kk\rangle \leftarrow |Nn\rangle$. N resp. K describes the electronic ground resp. excited state and n resp. k the vibrational state in N resp. K. $\omega_{KkNn} = 1/\hbar$ $(E_{Kk} - E_{Nn})$; $\langle \mu_r \rangle_{NnKk}$ resp. $\langle C_{sj} \rangle_{NnKk}$ is the electric dipole resp. quadrupole transition moment; $\langle m_r \rangle_{NnKk}$ is the magnetic dipole transition moment. $\varepsilon_{123} = \varepsilon_{312} = \varepsilon_{231} = 1$; $\varepsilon_{132} = \varepsilon_{213} = \varepsilon_{321} = -1$; all other tensor coordinates ε_{ijk} are zero. g_{ij33} are the orientational distribution coefficients defined by

$$g_{ijkl} = \frac{1}{8\pi^2} \int f(a,\beta,\gamma) a_{ik} a_{jl} \sin\beta \, da \, d\beta \, d\gamma. \tag{3}$$

$f(a,\beta,\gamma)$ represents the orientational distribution as a function of the Eulerian angles [1] and a_{ij} describes the transformation from the laboratory (x_i') to the body-fixed (x_i) coordinate system. If the CD. is measured for an uniaxial sample, as described in section 3, the orientational distribution can be approximated by a superposition of a system of oriented molecules (fraction ρ) and a system of isotropically distributed molecules (fraction $1-\rho$). The oriented molecules are with their x_3 axis aligned completely parallel to the optical axis of the uniaxial sample and distributed equally about this axis. The quantitative description (*Fraser* model) is given by

$$f(a,\beta) = 1 - \rho + \rho \frac{4\pi}{\sin\beta} \delta(a - a_0) \delta(\beta - \beta_0). \tag{4)^2}$$

For this type of the function $f(a,\beta,\gamma)$ only diagonal elements of R_{ij}^{NnKk} contribute to $\Delta\varepsilon^A(\tilde{v})$:

$$\Delta\varepsilon^A(\tilde{v}) = g_{1133}\Delta\varepsilon_{11}^A(\tilde{v}) + g_{2233}\Delta\varepsilon_{22}^A(\tilde{v}) + g_{3333}\Delta\varepsilon_{33}^A(\tilde{v}) \tag{5a}$$

$$\Delta\varepsilon_{\beta\beta}^A(\tilde{v}) = B\tilde{v} \sum_n \sum_{Kk} R_{\beta\beta}^{NnKk} G^{NnKk}(\tilde{v}) \tag{5b}$$

$$(\beta = 1, 2, 3; \text{ no summation over } \beta)$$

Using equ. (4) and (5) the following explicit equation results:

$$\Delta\varepsilon^A(\tilde{v}) = \left\{ \frac{1}{3} + \frac{1}{6}\rho(3\sin^2\beta_0 - 2) \right\} \left(\Delta\varepsilon_{11}^A(\tilde{v}) + \Delta\varepsilon_{22}^A(\tilde{v}) \right)$$

$$+ \left\{ \frac{1}{3} - \frac{1}{3}\rho(3\sin^2\beta_0 - 2) \right\} \Delta\varepsilon_{33}^A(\tilde{v}) \tag{6a)^2}$$

and for $\beta_0 = 0$:

$$\Delta\varepsilon^A(\tilde{v}) = (1 - \rho)\Delta\varepsilon_{iso}(\tilde{v}) + \rho\Delta\varepsilon_{33}^A(\tilde{v}) \tag{6b)^2}$$

For both equations we have assumed that the light is travelling parallel to the laboratory fixed x_3' direction, which is parallel to x_3 under the condition chosen for equ. (6b). $\Delta\varepsilon_{11}^A(\tilde{v})$, $\Delta\varepsilon_{22}^A(\tilde{v})$ and $\Delta\varepsilon_{33}^A(\tilde{v})$ is the CD. measured with a light wave
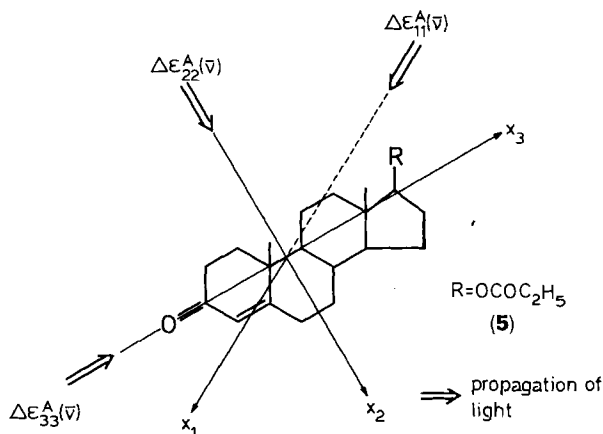
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[2]   See footnote page 574.

Fig. 1. *CD. measured in different directions of the molecule.*

propagating parallel to the x_i-axes of the molecules aligned completely parallel to each other *(Fig. 1)*. x_3 is the assumed orientation axis of the molecules, which, in general, does not coincide with an axis of the system of principal axes of the tensor $\sum_n \sum_{Kk} R_{ij}^{NnKk} G^{NnKk}(\tilde{v})$. Therefore the diagonal elements given in equ. (5) are not the eigenvalues of the latter tensor. The CD. $\Delta\varepsilon_{\beta\beta}^{A}(\tilde{v})$ measured parallel to the axis x_β ($\beta = 1, 2, 3$) is invariant against a rotation of the molecules about this axis. Furthermore, as can be seen from equ. (6a), a rotation of 180° around the x_1 axis does not change the measured effect $\Delta\varepsilon^{A}(\tilde{v})$. That means that the CD. for a molecule with its carbonyl group parallel or antiparallel to the x_3 direction is the same. This statement is important if the orientation is produced in a liquid crystal, because there both orientations are equally probable. For this the orientational distribution function is given by[3])

$$f(a,\beta) = 1 - \rho + \rho \frac{2\pi}{\sin\beta}\{\delta(a-a_0)\delta(\beta-\beta_0) + \delta(a-a_0-\pi)\delta(\beta-\beta_0-\pi)\}.$$

Using this equation for the evaluation of g_{ijkl} results in equations for $\Delta\varepsilon^{A}(\tilde{v})$ resp. $\varepsilon_\beta(\tilde{v})$ ($\beta = 1,2$) which are of identical form as equ. (6b) resp. equ. (8a) and (8b).

1.2. *The UV. spectra.* As developed in the paper III [4] the absorption for a light wave polarized parallel to the $x_1' x_3'$ resp. $x_2' x_3'$ plane and propagating in the x_3' direction is given by ε_1 resp. ε_2:

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[3]) Equ. (4) and this equation, which represents a symmetrical *Fraser* distribution, are special approximations of the real orientational distribution function of the experimental system. One could think that the results depend on the choice of the special distribution function but this is not the case. If for instance the symmetrical *Fraser* distribution is chosen, only the value of the parameter $\rho = \langle P_2 \rangle$ [2] determines the result for $\Delta\varepsilon^{A}(\tilde{v})$ and $\varepsilon_\beta(\tilde{v})$. Any other symmetrical distribution *e.g.* the *Maier-Saupe* distribution, with the same $\langle P_2 \rangle$, would give the same result [3].

$$\varepsilon_1(\tilde{v}) = g_{ij11}\varepsilon_{ij}(\tilde{v}) \tag{7a}$$

$$\varepsilon_2(\tilde{v}) = g_{ij22}\varepsilon_{ij}(\tilde{v}) \tag{7b}$$

$$\varepsilon_{ij}(\tilde{v}) = \frac{B\,\tilde{v}}{4}\sum_{n}\sum_{Kk} D_{ij}^{NnKk}\, F^{NnKk}(\tilde{v}) \tag{7c}$$

B is given in equ. (1b) and g_{ijkl} is defined by equ. (3). D_{ij}^{NnKk} represents the tensor of the transition moment and $F^{NnKk}(\tilde{v})$ is the spectral function of the transition $|Kk\rangle \leftarrow |Nn\rangle$. Using equ. (4) and the special conditions $a_0 = 0$ and $\beta_0 = \pi/2$ the following equ. (8a), (8b) and (8c) can be derived[4]:

$$\varepsilon_1(\tilde{v}) = (1-\rho)\,\varepsilon_{\mathrm{iso}}(\tilde{v}) + \rho\,\varepsilon_{33}(\tilde{v}) \tag{8a)^2}$$

$$\varepsilon_2(\tilde{v}) = \left(1+\frac{\rho}{2}\right)\varepsilon_{\mathrm{iso}}(\tilde{v}) - \frac{\rho}{2}\,\varepsilon_{33}(\tilde{v}) \tag{8b)^2}$$

$$\varepsilon_{\mathrm{iso}}(\tilde{v}) = \frac{1}{3}\left(\varepsilon_{11}(\tilde{v}) + \varepsilon_{22}(\tilde{v}) + \varepsilon_{33}(\tilde{v})\right) \tag{8c}$$

Furthermore the degree of polarization can be calculated as follows:

$$P = \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} = \frac{3\rho\left\{\varepsilon_{33} - \dfrac{1}{2}(\varepsilon_{11}+\varepsilon_{22})\right\}}{2(\varepsilon_{11}+\varepsilon_{22}+\varepsilon_{33}) + \rho\left\{\varepsilon_{33} - \dfrac{1}{2}(\varepsilon_{11}+\varepsilon_{22})\right\}} \tag{9}$$

2. The problem. – In the preceding paper [4] it has been shown by the mechanism of vibronic coupling that different progressions of vibrations contribute to various amounts to the CD. measured with light propagating in the different directions within the molecule *i.e.* to $\Delta\varepsilon_{11}^A$, $\Delta\varepsilon_{22}^A$ and $\Delta\varepsilon_{33}^A$. For this each tensor coordinate has to be multiplied with a spectral function of different type and therefore the $\Delta\varepsilon_{\beta\beta}^A$ ($\beta = 1, 2, 3$) will be of different form and magnitude *(Fig. 2a)*. Therefore $\Delta\varepsilon^A(\tilde{v})$ will generally depend on the magnitude of the coefficients g_{ijkl} (equ. (5)), which are determined by the type of the orientational distribution function. Using the *Fraser* model, $\Delta\varepsilon^A(\tilde{v})$ will be a function of ρ (equ. (6)) as demonstrated in *Figure 2b*. If the optically active molecule is solved in an oriented mesophase, the orientational distribution function and therefore ρ is a function of the concentration of the solute and of the temperature. This has been shown experimentally by different methods *e.g.* NMR. measurements [5]. Therefore the magnitude and band structure of $\Delta\varepsilon^A(\tilde{v})$ should be a function of the concentration of the solute and of the temperature.

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[4]   For the oriented fraction of molecules, the molecular axis x_3 is chosen to be parallel to the x_1' axis, which is defined for the absorption measurement to be the optical axis of the uniaxial system. The direction of propagation is parallel to x_3'.
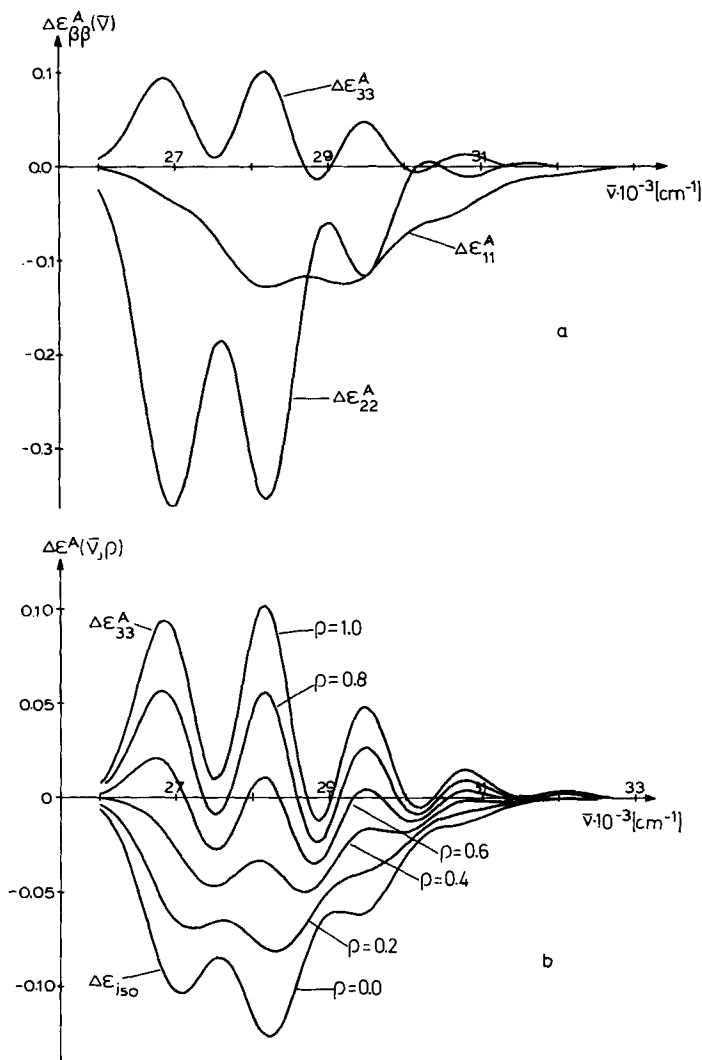
Fig. 2. a) $\Delta\varepsilon^A_{\beta\beta}(\tilde{\nu})$ curves calculated (equ. (6b)) by a formalism developed within the Herzberg-Teller method; b) $\Delta\varepsilon^A(\tilde{\nu})$ as a function of the order parameter ρ, using the data of Fig. 2a.

In this paper, the experimental proof will be given for testosterone propionate that the C.D. connected with different tensor coordinates has a different frequency dependence. The vibrational structure, the concentration and temperature dependence will be analysed.

3. Experimental Part. – $\Delta\varepsilon^A(\tilde{\nu})$, $\varepsilon_1(\tilde{\nu})$ and $\varepsilon_2(\tilde{\nu})$ are measured for the solution of testosterone propionate (**5**) in the mesophase of a mixture of cholesteryl chloride and cholesteryl laurate (1.8:1 by weight). The orientation of the solution is generated by a constant electric field $(2 \cdot 10^6 \text{ V/m})$. The thickness of the samples is mostly 1, sometimes 3 mm. Under this condition, no scattering of light can be seen visually. The compensated nematic phase of the pure mixture [6] exists in the region of

$T \simeq 36°$. The CD. resp. UV. spectra of the isotropic solution are measured at $T = 80°$. For all measurements the x_3' axis is defined as the direction of propagation of light. For the CD. measurements, the optical axis of the system is parallel to the x_3' axis (electric field parallel to x_3'). For the UV. measurements, the x_1' axis is chosen as the optical axis of the system (electric field parallel to x_1').

4. Results. – The CD. spectrum of testosterone propionate (**5**) in the isotropic solution of the mixture of cholesteryl chloride/cholesteryl laurate $(\Delta\varepsilon_{iso}(\tilde{v}); T = 80°)$ and in heptane for $T = 23°$, $36°$ and $80°$ are of the same structure and magnitude *(Fig. 3a)*. The small differences between the curves should be due to the usual solvent effect.

The measurement in the oriented mesophase $(\Delta\varepsilon^A(\tilde{v}); T = 36°)$ shows a strong alteration of the magnitude and band structure compared to $\Delta\varepsilon_{iso}(\tilde{v})$ *(Fig. 3c, d)*. These curves depend on concentration and temperature. The measurable range of concentration is determined for small concentrations by the sensitivity of the apparatus and the error produced by interference of linear birefringence. For concentrations higher than 0.3 mol l^{-1} the signal to noise ratio decreases in a way that every measurement was impossible, although visually the samples are as transparent as those with smaller concentration. The variation of temperature is limited by a resulting phase transition from the nematic to the cholesteric phase.
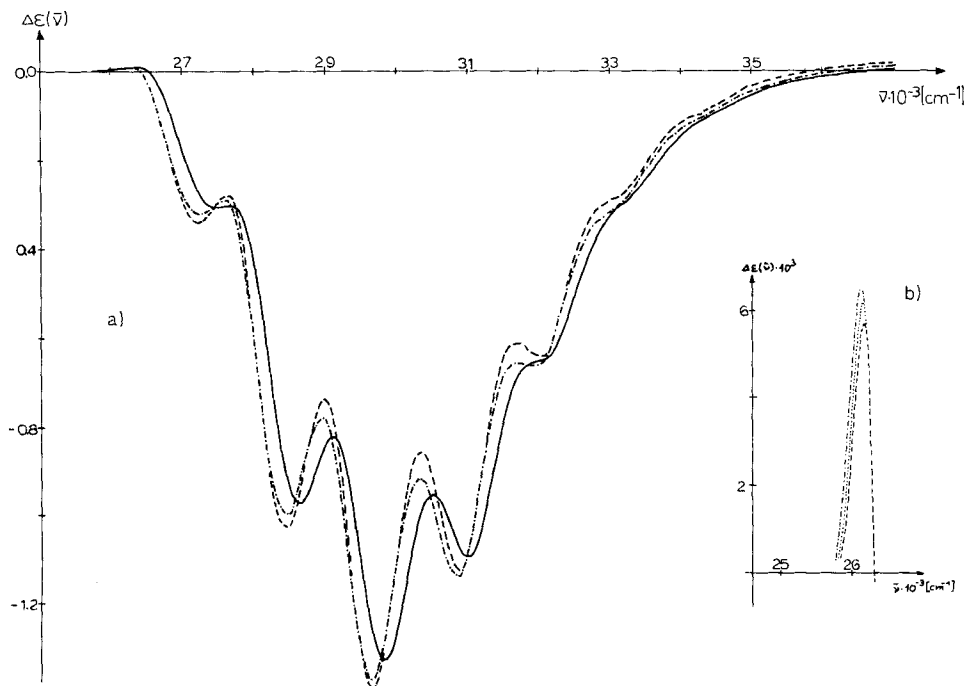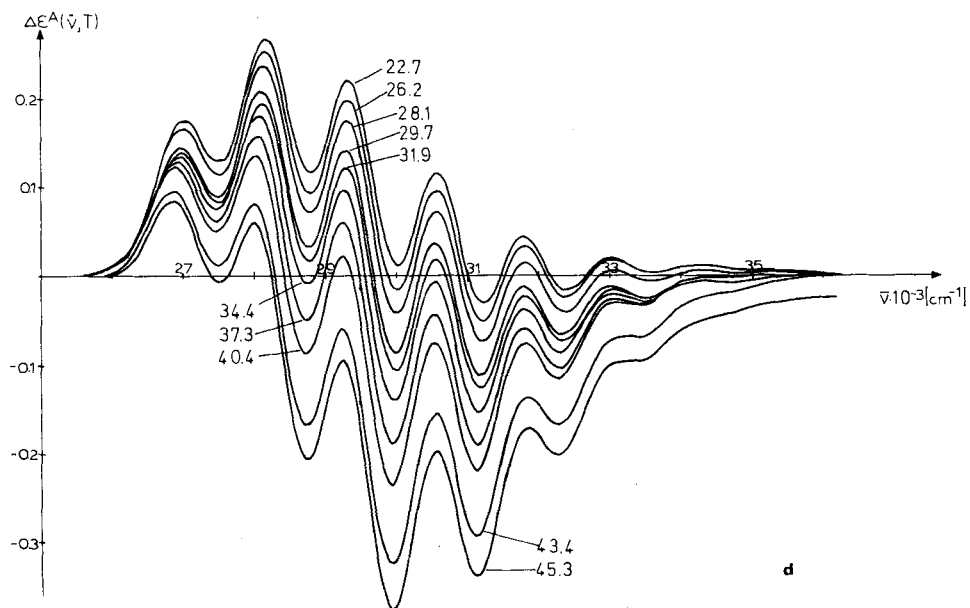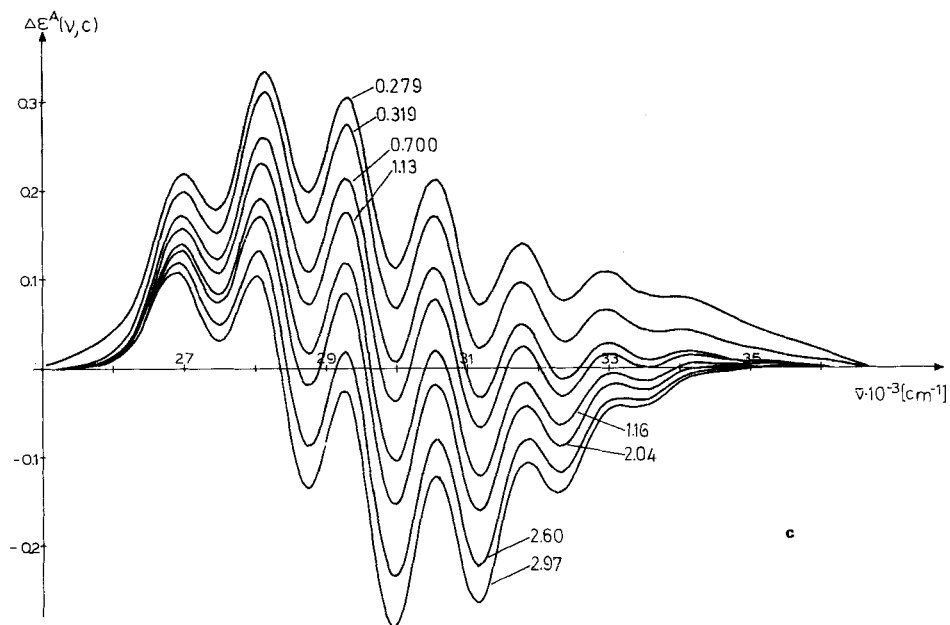

Fig. 3. a) $\Delta\varepsilon_{iso}(\tilde{v})$ (———) *of* **5** *in the liquid crystal mixture* (80°) *and the spectra* $\Delta\varepsilon(\tilde{v})$ *in heptane* [$T = 23°$ (– – – –); $T = 80°$(–·–··–·–·)]. (The spectrum for $T = 36°$ is omitted, because it is within the accuracy of the figure equal to that of $T = 23°$).
b) *The small positive CD. band at* $\tilde{v} = 26.180$ cm^{-1} *in heptane and its temperature dependence* [$T = 23°$ (– – – –); $T = 36°$ (·········); $T = 80°$ (–·–··–·–·)]

c) *The concentration dependence of $\Delta \varepsilon^A(\tilde{v})$ of **5** in the oriented liquid crystal matrix* (T = 35.3°; parameter $c \cdot 10 \text{ mol l}^{-1}$)

d) *The temperature dependence $\Delta \varepsilon^A(\tilde{v})$ of **5** in the oriented liquid crystal matrix* ($c = 0.2026 \text{ mol l}^{-1}$ at T = 35.3°; parameter T °C)

Within the experimental error the change of $\Delta\varepsilon^A(\tilde{v})$ as a function of temperature and of concentration respectively is the same at each wave number. That means $d\,\Delta\varepsilon^A(\tilde{v})/d\,c$ is proportional to $d\,\Delta\varepsilon^A(\tilde{v})/d\,T$ for each wave-length.

The UV. spectrum of **5** in the isotropic solution of the cholesteryl chloride/ cholesteryl laurate mixture is the same as that in heptane apart from a small solvent dependence. The concentration and temperature dependence show the same behaviour as the CD. spectra. The degree of polarization as a function of $\tilde{v}$ is not uniform *(Fig. 4)*.

5. Discussion. – It is known [7] from UV., NMR., ESR. and other methods that a solute can be oriented in a liquid crystal matrix, which is oriented itself in an electric field. Therefore the measured effect in UV. and CD. should be a consequence of an anisotropic orientational distribution. But there can also be a solvent effect because the surroundings of the solute are different in the isotropic solution and in the oriented mesophase. Beside the intensity change $(\Delta\varepsilon(\tilde{v}); \varepsilon(\tilde{v}))$ and the shift of wave-length of the bands, a change of the spectra due to the different contributions of the three possible conformers [8] of **5** can occur. Furthermore, in the following discussion we have to compare measurements of the isotropic and anisotropic solutions which are done at different temperatures. For this we have to analyse the temperature effect in order to estimate the magnitude with which this effect contributes to the change from $\Delta\varepsilon_{iso}(\tilde{v})$ to $\Delta\varepsilon^A(\tilde{v})$.

5.1. *The temperature and solvent effect.* Both the temperature and the solvent effect of the UV. and the CD. spectra are relatively small *(Fig. 3a, 4b)*. Lowering the temperature from 80° to 36° results in an increase of the CD. of about 7 to 8% in the main bands (negative bands) and in the small positive band at the long wave-length side *(Fig. 3b)*. The whole alteration can be interpreted as a very small shift of the CD. from a positive to a negative sign. This shift is small but similar as compared to the change of the band structure in the isotropic-anisotropic transition. Therefore both effects could have the same origin.

Assuming the existence of some conformers the mean value of the CD. is given by[5]

$$\frac{\Delta E}{c_0 d} = \overline{\Delta\varepsilon}_{iso}(\tilde{v}) = \frac{\sum_i K_{i1}\Delta\varepsilon_i(\tilde{v})}{\sum_i K_{i1}}\;. \tag{10}$$

K_{ij} is the equilibrium constant for the equilibrium between the conformers i and j $(K_{ij} = c_i/c_j)$ and c_0 the weight-in quantity. $\overline{\Delta\varepsilon}_i(\tilde{v})$ represents the CD. of the conformer i. If one assumes that only two conformers are essential, then the change of $\Delta\varepsilon_{iso}(\tilde{v})$ as a function of K_{ij} and therefore as a function of temperature can be described with an equation identical to equ. (6b), if ρ is interpreted as: $\rho = K_{21}/(1 + K_{21})$. Using $\Delta\varepsilon_i$-values for the two conformers which have a different sign, a change of the curve similar to *Figure 2b* can be constructed. Comparison of the measured temperature dependence of $\Delta\varepsilon_{iso}(\tilde{v})$ and that of $\Delta\varepsilon^A(\tilde{v})$ with the theoretical curves $\Delta\varepsilon^A(\tilde{v}.\rho)$ in *Figure 7* shows that this mechanism seems to be unimportant. One can draw a similar conclusion from the UV. spectra. The solvent effect for a series of nonpolar and polar solvents leads to the same result [9]. Therefore, temperature and solvent effects are only of subordinate importance. By neglecting these effects the error of the calculated data given in the following sections should be small, probably not larger than 8%.

5.2. *Estimation of the order parameter ρ and the direction of the transition moment.* As mentioned in paper III [4], it is impossible to determine ρ in general from equ. (8) only with the knowledge of $\varepsilon_{iso}(\tilde{v})$, $\varepsilon_1(\tilde{v})$ and $\varepsilon_2(\tilde{v})$ and any further measurement of the absorption with light having an oblique direction of propaga-

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[5]) $\overline{\Delta\varepsilon}_{iso}(\tilde{v})$ is independent of the concentration (weight-in quantity) of the solution.
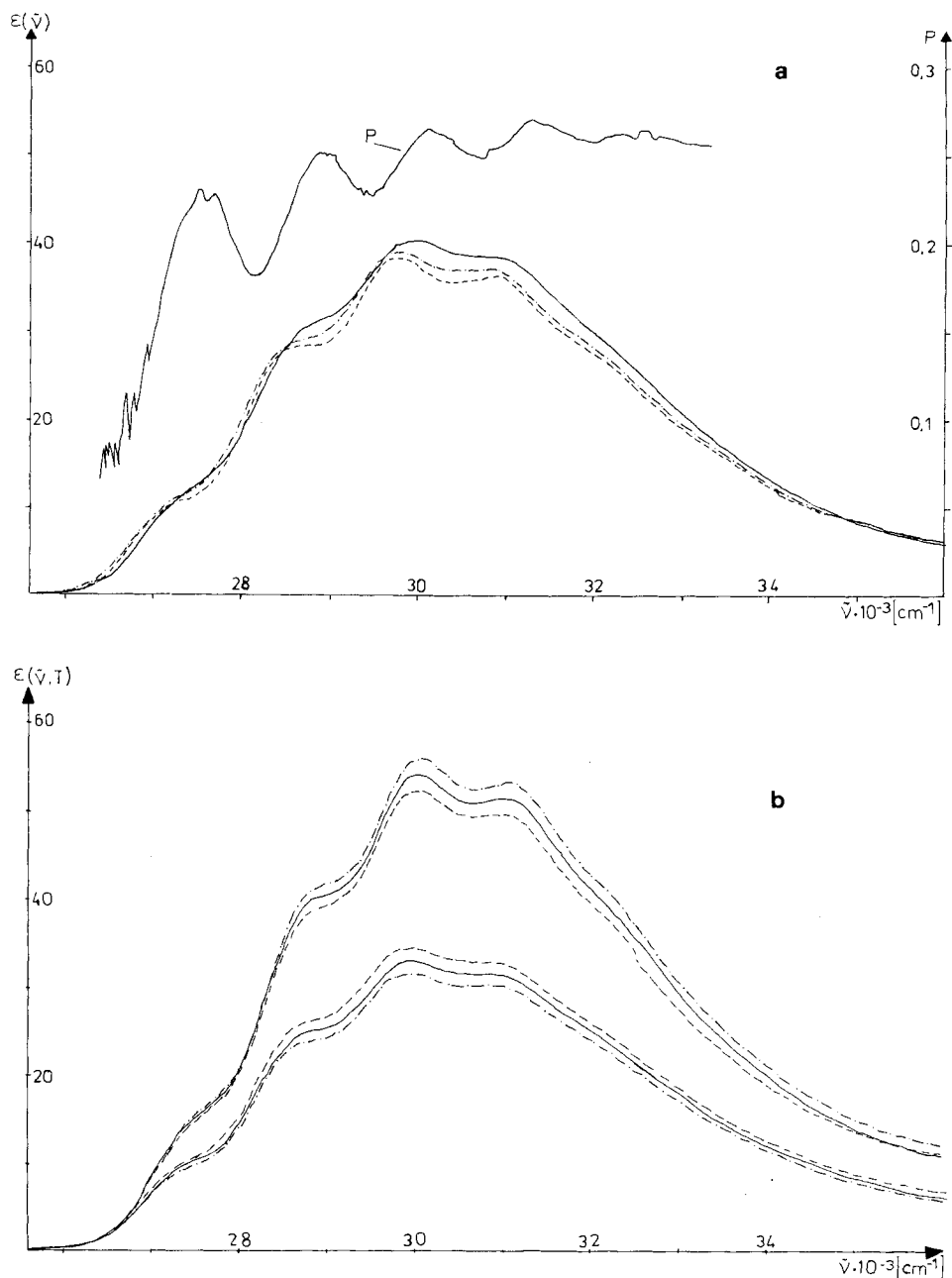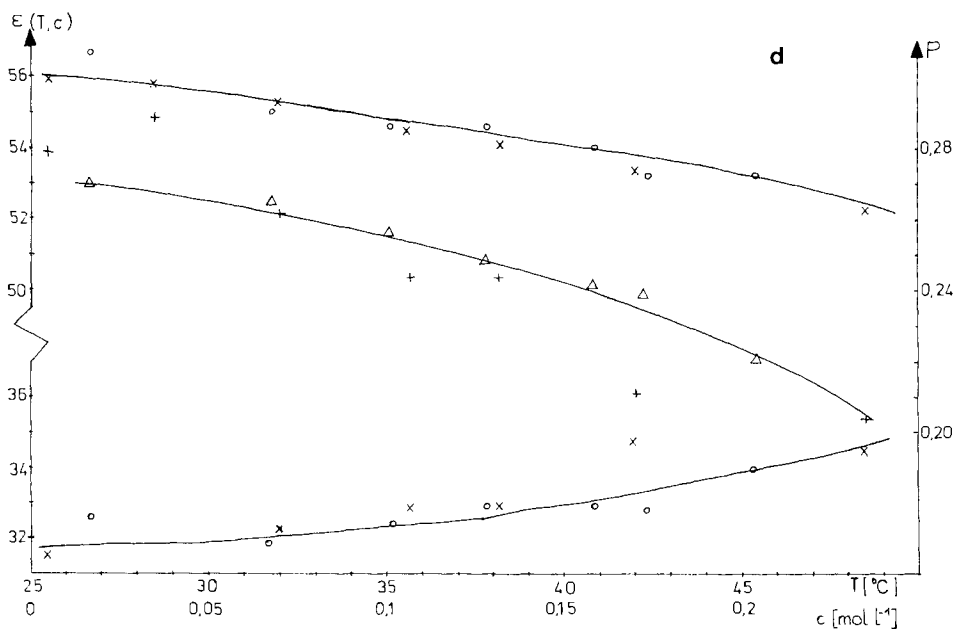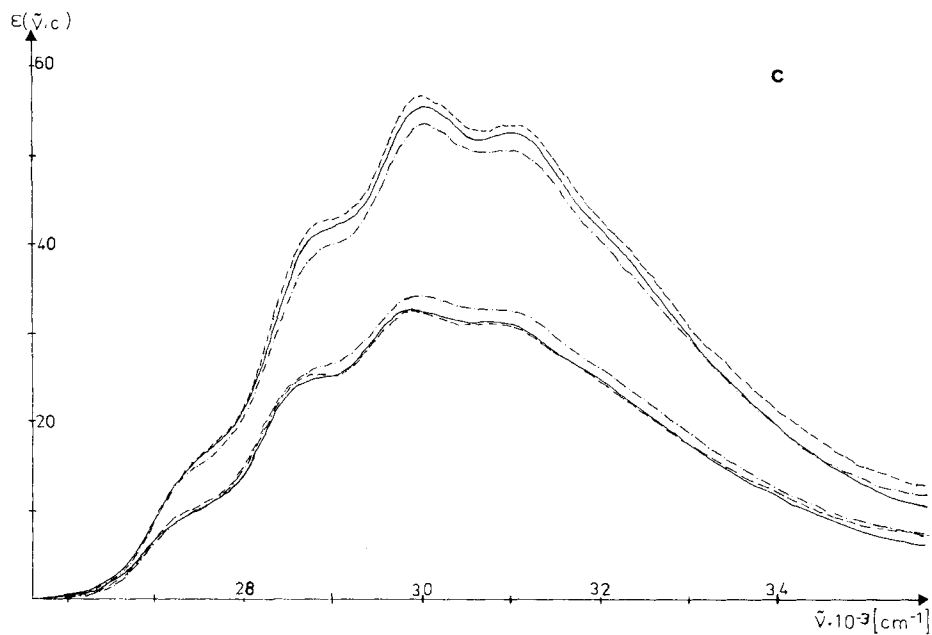
Fig. 4. a) $\varepsilon_{iso}(\tilde{v})$ *of* **5** *in the liquid crystal mixture* (T = 81° (———)), *the degree of polarization* (T = 38.2°) *and* $\varepsilon(\tilde{v})$ *in heptane* (T = 23° (----); T = 81° (-·--·-·--·--));

b) *The anisotropic absorption* $\varepsilon_1(\tilde{v})$ *and* $\varepsilon_2(\tilde{v})$ *of* **5** (c = 0.01732 (----) c = 0.0682 (———) c = 0.20443 (-·--·-·--·--) mol l^{-1}; T = 38.2°);

ε_1 are the three upper, ε_2 the three lower curves.

c) *The anisotropic absorption $\varepsilon_1(\tilde{v})$ and $\varepsilon_2(\tilde{v})$ of* **5** (T = 25.5° (–·–·–·–·–·–·); T = 38.2° (–———); T = 48.5° (– – – –); c = 0.185 at T = 35.6°); ε_1 are the three upper, ε_2 the three lower curves;

d) *The anisotropic absorption $\varepsilon_1(\tilde{v}_0)$ [upper curve] and $\varepsilon_2(\tilde{v}_0)$ [lowest curve] and the degree of polarization $P(\tilde{v}_0)$ as a function of the concentration and temperature* [$\tilde{v}_0 = 30.030$ cm^{-1}; for f(T): [x, +] c = 0.186 mol/l; for f(c) [o, △] T = 38.2°].

tion with respect to the optical axis of the system. In addition to these quantities, one has to know the value of $\varepsilon_{11} + \varepsilon_{22}$ or ε_{33}, which in general is not accessible. In order to overcome this problem, more or less severe simplifications are necessary. For determining ρ and the direction of the transition moment for **5** we have to combine the UV.-data of three different compounds: **2**, **5** and **8** (Fig. 5). Furthermore, we need the following assumptions:

a) The transition moment of **2**, **5** and **8** is determined by the same chromophor $C=C-C=O$. Its direction is connected for all three molecules in the same way to the skeleton of the chromophor and is – as well as the absolute value of $\langle \mu_r \rangle_{NnKk}$ – independent of the other parts of the molecule;

b) The transition moment lies in the $x_2 x_3$ plane defined by the condition $\varepsilon_{11} = 0$. This plane should be essentially the "mean" plane of the molecule (Fig. 5);

c)[6]) The axis of orientation given by x_3 is the same in **2, 5** and **8**;

d)[6]) The order parameter ρ is the same for the three molecules because the structure of these molecules is very similar;

e) The skeleton of the chromophor of **2** and therefore the transition moment transforms to that of **8** by a rotation of

$$\gamma_{8/2} = \sigma_8 - \sigma_2 = 240° ;$$

f) The skeleton of the chromophor of **8** and therefore the transition moment transforms to that of **5** by the mirror plane $x_1 x_3$ ($\sigma' = \sigma''$ in Fig. 5). For that reason the angle between the directions of the two transition moments of **2** and **5** is given by

$$\gamma_{5/2} = \sigma_5 - \sigma_2 = 2(390 - \sigma_8) .$$

With the assumptions a) and b) one gets:

$$\varepsilon_{11} = 0$$

$$\varepsilon_{22} = 3 \, \varepsilon_{iso} \cos^2 \sigma \qquad (11)[7])$$

$$\varepsilon_{33} = 3 \, \varepsilon_{iso} \sin^2 \sigma$$

σ is the angle between the transition moment and the x_2 axis. From equ. (8) and (11) the absorption coefficients are

$$\varepsilon_1 (\tilde{\nu}) = 3 \, \varepsilon_{iso} (\tilde{\nu}) \left\{ \frac{1}{3} (1 - \rho) + \rho \sin^2 \sigma (\tilde{\nu}) \right\} \qquad (12\,a)$$

$$\varepsilon_2 (\tilde{\nu}) = 3 \, \varepsilon_{iso} (\tilde{\nu}) \left\{ \frac{1}{3} (1 - \rho) + \frac{\rho}{2} \cos^2 \sigma (\tilde{\nu}) \right\} . \qquad (12\,b)$$

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[6]) From CD. measurements one can see that this is not really true [3]. But because there is only a relatively low sensitivity of the UV. spectra against rotations of the molecule, this assumption is allowed here.
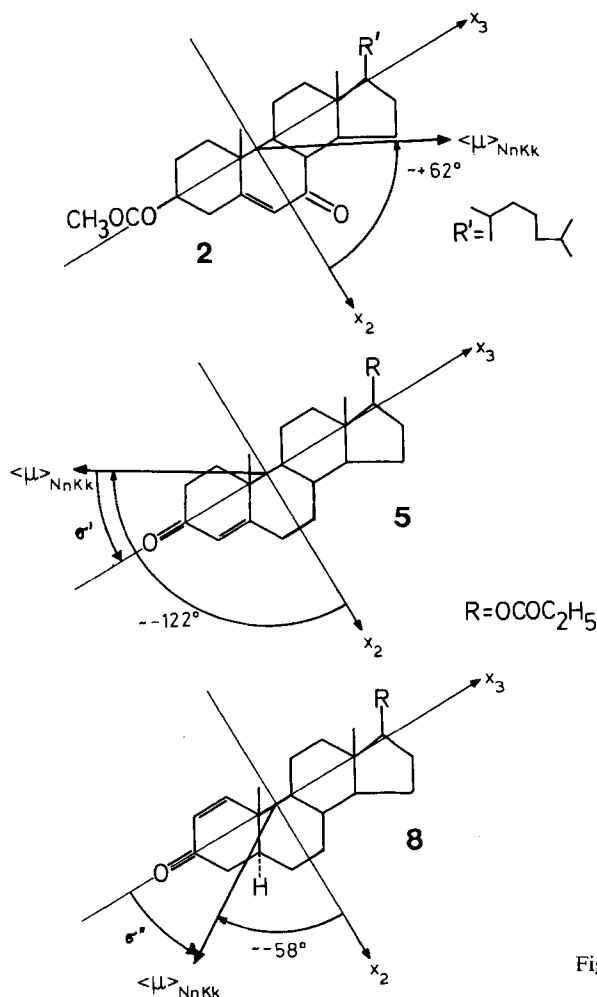
[7]) σ is a function of $\tilde{\nu}$.

Fig. 5. *Comparison of the different directions of the transition moments in* **2**, **5** *and* **8**

With the simplifications c) and d) and the equ. (12) the direction of the transition moment for the ith compound ($i \neq 2$) is given by:

$$\operatorname{tg}\sigma_i = \frac{\dfrac{3}{2}\sin 2\,\gamma_{i/2} \pm \sqrt{2\left(1-\dfrac{R_2}{R_i}\right)^2 + 9\,\dfrac{R_2}{R_i}\sin^2\gamma_{i/2}}}{2\left(1-\dfrac{R_2}{R_i}\right) - 3\sin^2\gamma_{i/2}} \qquad (13\,a)^{8)}$$

$$\sigma_2 = \sigma_i - \gamma_{i/2} \qquad\qquad (13\,b)$$

$R_i = [(\varepsilon_1 - \varepsilon_2)/(\varepsilon_1 + 2\,\varepsilon_2)]_i$ is the degree of anisotropy of the ith compound.

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[8]   In order to fulfill the condition $0 \le \rho \le 1$, we have used here the positive sign in equ. (13a).

Using the compound **2** as a reference (the UV. data are given in [10]) the transition moment of **8** can be calculated by equ. (13 a) because $\gamma_{8/2}$ is known. From σ_8 and equ. (14) the parameter σ can be calculated from the UV. data of **8** [11]. Using UV. data from different wave numbers a set of p values is obtained. A second set can be evaluated with

$$p = \frac{2\,R_i}{3\sin^2\sigma_i - 1} \tag{14}$$

from the UV. data of **5** *(Fig. 4)* and the transition moment of **8**, obtained by the relation between $\gamma_{5/2}$ and σ_8. Because of the concentration dependence of $\varepsilon_1(\tilde{\nu})$ and $\varepsilon_2(\tilde{\nu})$, we choose for evaluating σ and p measurements done with nearly the same concentration ($\simeq 6 \cdot 10^{-2}\,\mathrm{mol}\,\mathrm{l}^{-1}$). Because of the conditions a) and b) and the fact that the UV. spectra of different compounds are slightly shifted against each other we have always used for the calculations with equ. (13 a) and (14) absorption coefficients, which belong to wavenumbers having the same distance to the maximum of the UV. band of each compound.

From the UV. data of **2**, **5** and **8** in the spectral region of about 28,000 to 33,000 cm^{-1} the order parameter is given by $p = 0.27$. It is very difficult to estimate the error of this number. Because of the severe simplifications of the method one has to expect an error of 25–30%. More important – and this we have to point out very clearly – is the fact that we do not get any information about the absolute orientation of the coordinate axes within the molecule for unsymmetrical compounds as **2, 5** and **8**.

5.3. *The tensor of rotation and the concentration and temperature dependence of the order parameter p.* Using the order parameter determined from the UV.-spectra, the tensor coordinate $\sum_n \sum_{Kk} R_{33}^{NnKk}\,G^{NnKk}(\tilde{\nu})$ resp. $\Delta\varepsilon_{33}^A(\tilde{\nu})$ can be calculated by equ. (6) from the measured curves of $\Delta\varepsilon^A(\tilde{\nu})$ and $\Delta\varepsilon_{iso}(\tilde{\nu})$[9]. From these numbers the sum of $\Delta\varepsilon_{11}^A(\tilde{\nu})$ and $\Delta\varepsilon_{22}^A(\tilde{\nu})$ can be evaluated too, which is shown together with $\Delta\varepsilon_{33}^A(\tilde{\nu})$ in *Figure 6*. This is the experimental proof for the statement given in paper III [4] that the spectral functions of the CD. connected with different tensor coordinates have a different frequency dependence.

With these data one can calculate $\Delta\varepsilon^A(\tilde{\nu})$ as a function of p *(Fig. 7)*. The good agreement all over the frequency region between the structure of the calculated and the measured curves gives a further evidence for the correctness of the model used. Comparison with the concentration and temperature dependent experimental curves allows a quantitative determination of $p\,(T)$ and $p\,(c)$ as given in *Figure 8*. From this it seems that the CD. measurement of the compound **5** gives a very sensitive method for determining the concentration and temperature dependence of p. The same analysis as discussed for the CD. data can be done for the UV. absorption spectra *(Fig. 4)*. The components of the absorption spectrum are given in *Figure 9*. From this the order parameter p can be calculated too but the accuracy is lower here. The reason for this higher sensitivity in deriving p from the CD. instead of the UV. spectra is given by the different signs of the terms in equ. (6) $\left(i.e.\ \Delta\varepsilon_{33}^A(\tilde{\nu})\ \text{and}\ \Delta\varepsilon_{iso}^A(\tilde{\nu})\right)$.

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[9]) $\Delta\varepsilon_{iso}(\tilde{\nu})$ is defined by equ. (5) together with $g_{ij33} = 1/3\,\delta_{ij}$.
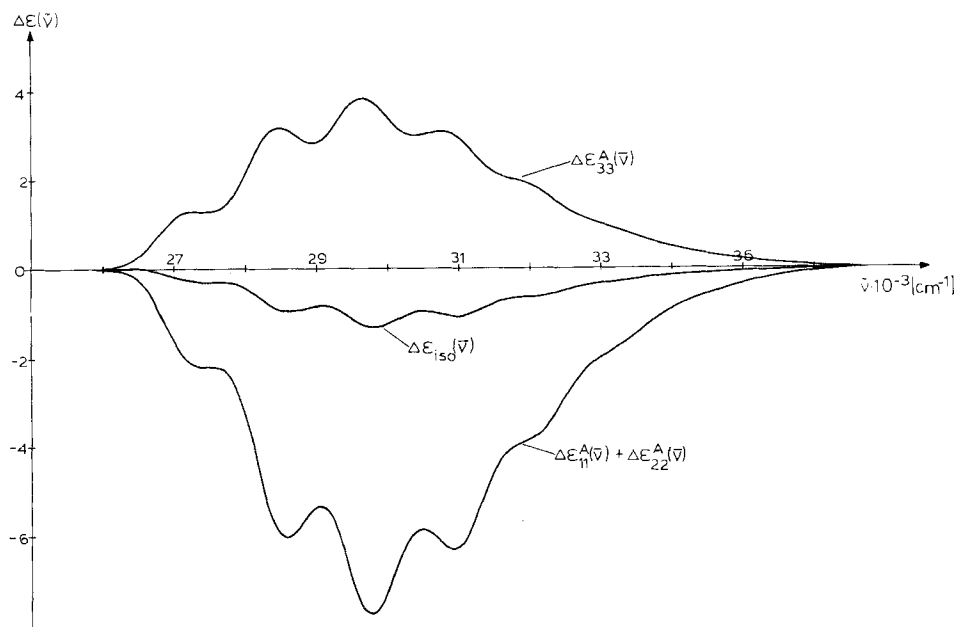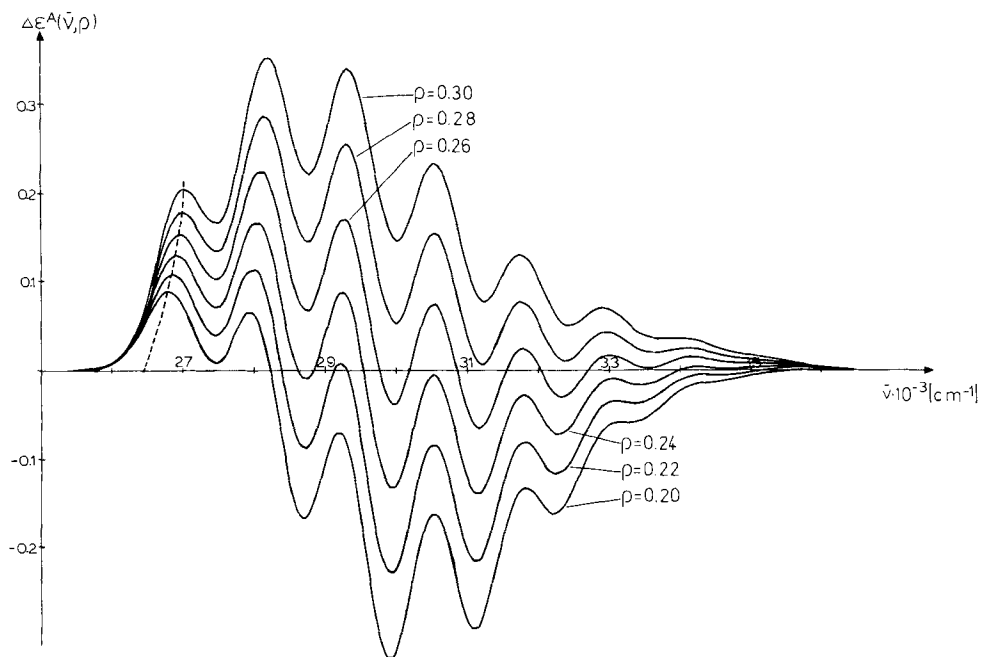
Fig. 6. *The calculated components of the CD. of* **5**

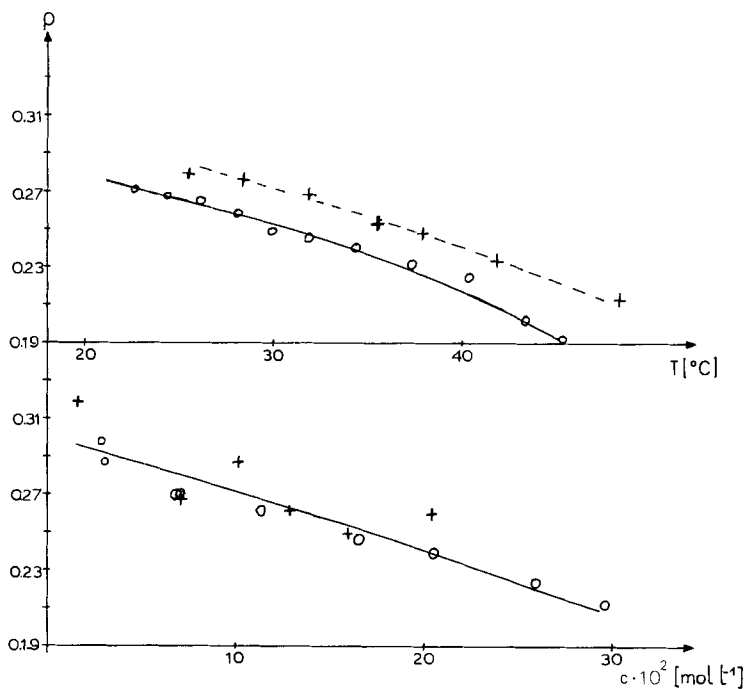Fig. 7. *The calculated $\Delta\varepsilon^A(\tilde{\nu})$ as a function of the order parameter*

Fig. 8. *The order parameter* ρ *as a function of the temperature and the concentration calculated from the CD:*($\bigcirc$)*and UV.* (+) *data*
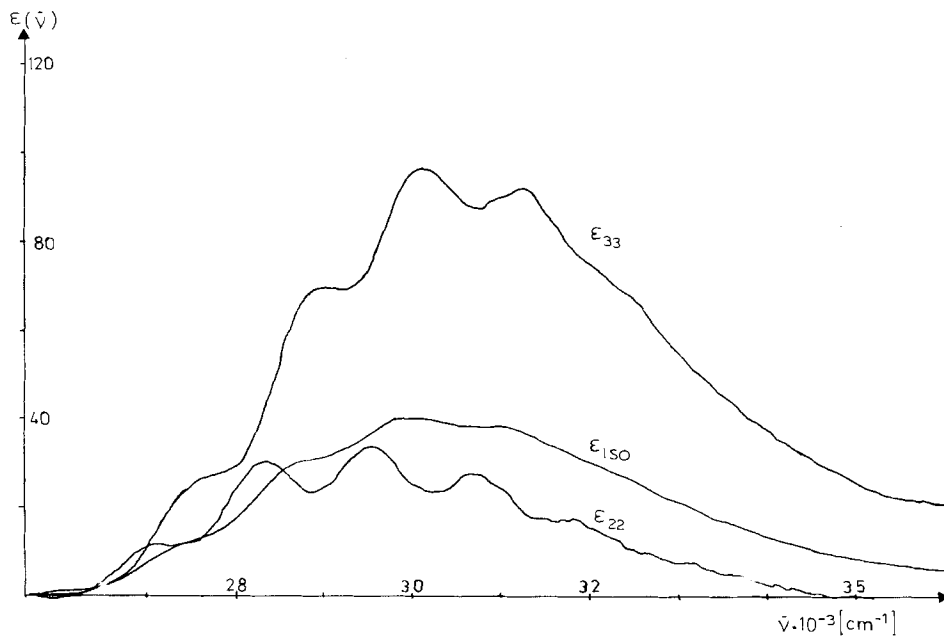

Fig. 9. *The calculated components of the UV. spectrum of* **5**

5.4. *Analysis of the vibrational structure.* It is shown in the preceding sections that the CD. connected with the various tensor coordinates has in each case a different frequency dependence. In a theoretical description using the *Herzberg-Teller* scheme [4], this behaviour originates in the fact that different modes of vibrations contribute by a different amount to $\Delta\varepsilon_{\beta\beta}$ ($\beta = 1, 2, 3$; no summations over β). Therefore a further separation resp. a decomposition of the bands $\Delta\varepsilon_{11}^{A}(\tilde{\nu}) + \Delta\varepsilon_{22}^{A}(\tilde{\nu})$ and $\Delta\varepsilon_{33}^{A}(\tilde{\nu})$ into different modes of vibrations should be possible.

Using the condition $\langle\mu_1\rangle = 0$, which results from the definition of the coordinate system (sect. 5.2), the explicit form of the tensor coordinates R_{ij}^{NnKk} is given by

$$R_{11}^{NnKk} = \langle\mu_2\rangle_{NnKk} \left\{ -\frac{i}{2} \langle m_2\rangle_{KkNn} - \frac{\omega_{KkNn}}{4c} \langle Q_{31}\rangle_{KkNn} \right\}$$

$$+ \langle\mu_3\rangle_{NnKk} \left\{ -\frac{i}{2} \langle m_3\rangle_{KkNn} + \frac{\omega_{KkNn}}{4c} \langle Q_{21}\rangle_{KkNn} \right\} \qquad (15\,a)$$

$$R_{22}^{NnKk} = \langle\mu_3\rangle_{NnKk} \left\{ -\frac{i}{2} \langle m_3\rangle_{KkNn} - \frac{\omega_{KkNn}}{4c} \langle Q_{12}\rangle_{KkNn} \right\} \qquad (15\,b)$$

$$R_{33}^{NnKk} = \langle\mu_2\rangle_{NnKk} \left\{ -\frac{i}{2} \langle m_2\rangle_{KkNn} + \frac{\omega_{KkNn}}{4c} \langle Q_{13}\rangle_{KkNn} \right\} . \qquad (15\,c)$$

This shows that the CD. produced by R_{11}^{NnKk} and R_{33}^{NnKk} is determined by contributions of transitions polarized parallel to the x_2 axis $(\varepsilon_{22}(\tilde{\nu}))$. These bands are responsible for a negative degree of polarization or for relative minima in the function $P(\tilde{\nu})$. R_{11}^{NnKk} also can have contributions from positively polarized bands (parallel to x_3). R_{22}^{NnKk} is only determined by progressions polarized parallel to the x_3 axis $(P(\tilde{\nu}) > 0; \varepsilon_{33}(\tilde{\nu}))$. Therefore the maxima given by $\Delta\varepsilon_{33}^{A}(\tilde{\nu})$ are associated with the relative minima in the curve of the degree of polarization. Because this band system has its origin in a $n \to \pi^*$ transition ($A_1 \to A_2$ in C_{2v}), the negatively polarized bands (parallel to $\langle\mu_2\rangle_{NnKk}$) cannot include the 0,0-band. Therefore we have to conclude that $\Delta\varepsilon_{33}^{A}(\tilde{\nu})$ is connected with the following type of progressions:

$$\tilde{\nu} = \tilde{\nu}_{00} + \tilde{\nu}_x + m\,\tilde{\nu}_1 \qquad (16)$$

$R_{11}^{NnKk} + R_{22}^{NnKk}$ resp. $\Delta\varepsilon_{11}^{A}(\tilde{\nu}) + \Delta\varepsilon_{22}^{A}(\tilde{\nu})$ *(Fig. 6)* should also be determined by a progression of the type given by equ. (16). But to a large extent the sum should be determined by systems of bands polarized parallel to x_3 $[(|\langle\mu_3\rangle| > |\langle\mu_2\rangle|),$ *Figure 9*], which include the 0,0-transition [equ. (17)]:

$$\tilde{\nu} = \tilde{\nu}_{00} + m\,\tilde{\nu}_1 \qquad (17)$$

Therefore the maxima of $\Delta\varepsilon_{11}^{A}(\tilde{\nu}) + \Delta\varepsilon_{22}^{A}(\tilde{\nu})$ belong to the relative maxima of the degree of polarization.

From this scheme we can derive at least two different progressions. One of them is given by equ. (16) and is connected with a positive CD. The other one [equ. (17)], which includes the 0,0-transition, belongs to a negative CD.

The separations of the maxima of $\Delta\varepsilon_{11}^A(\tilde{\nu})+\Delta\varepsilon_{22}^A(\tilde{\nu})$, $\Delta\varepsilon_{33}^A(\tilde{\nu})$, $\varepsilon_{22}(\tilde{\nu})$ and $\varepsilon_{33}(\tilde{\nu})$ are in the order of 1200 cm^{-1}, which is found also for saturated ketones in connection with the symmetric carbonyl-group-stretch frequency. Comparing the band systems of $\Delta\varepsilon_{11}^A(\tilde{\nu})+\Delta\varepsilon_{22}^A(\tilde{\nu})$ with that of $\Delta\varepsilon_{33}^A(\tilde{\nu})$ one can see that the first system appears at higher wave numbers *(Fig. 6)*. In agreement with this observation the progression of $\varepsilon_{33}(\tilde{\nu})$, which belongs to $\Delta\varepsilon_{11}^A(\tilde{\nu})+\Delta\varepsilon_{22}^A(\tilde{\nu})$, is found at higher wave numbers, too. Therefore the band at the lowest wave number in the progression of $\varepsilon_{33}(\tilde{\nu})$ and $\Delta\varepsilon_{11}^A(\tilde{\nu})+\Delta\varepsilon_{22}^A(\tilde{\nu})$ cannot be the 0,0-transition and we have to conclude that this is to weak to be observed here.

From the separated CD. and UV. spectra *(Fig. 6* and *9)*, a progression for the components $\varepsilon_{33}(\tilde{\nu})$ and $\Delta\varepsilon_{11}^A+\Delta\varepsilon_{22}^A(\tilde{\nu})$[10]) can be derived *(Fig. 10b, c)*, which has to be connected with the relative maxima of the degree of polarization *(Fig. 10a)*. Therefore one can describe this progression by equ. (17) as discussed before. A progression belonging to the relative minima of P *(Fig. 10a)*, which has its origin in the vibronic coupling (equ. (16)), can be derived from $\varepsilon_{22}(\tilde{\nu})$ and $\Delta\varepsilon_{33}^A(\tilde{\nu})$ *(Fig. 10b, d)*. The mean values from both descriptions *(Fig. 10c, d)* are given in *Figure 10d*. From these values the wave number of the totally symmetric progression is calculated to be $\tilde{\nu}_1 = 1170$ cm^{-1}. Assuming that the first band of $\varepsilon_{33}(\tilde{\nu})$ is connected with
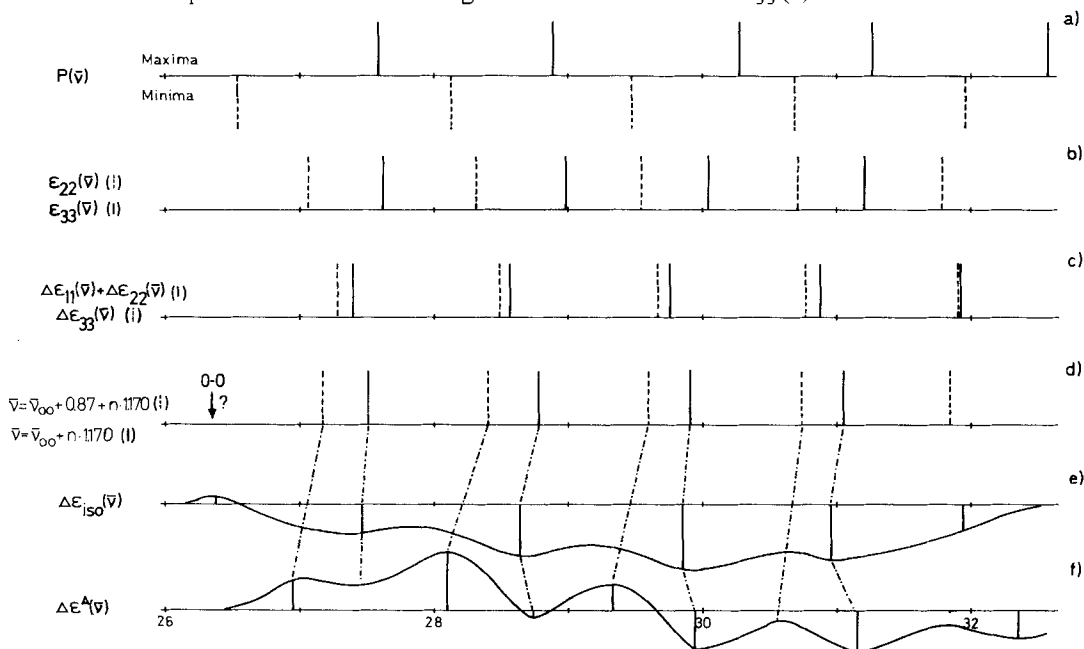

Fig. 10. *Analysis of the CD. and UV. spectra of* 5

[10]) A contribution to $\Delta\varepsilon_{11}^A(\tilde{\nu})+\Delta\varepsilon_{22}^A(\tilde{\nu})$ of the progression which is responsible for the spectrum of $\varepsilon_{22}(\tilde{\nu})$ cannot be seen in the experimental curve.

the first excited vibrational state (m = 1 in equ. (17)), then the 0,0-transition will be at 26,300 cm^{-1}. From this and the first band of the progression given by equ. (16), the 'nontotally symmetric' mode, which results from the vibronic coupling, is given by $\tilde{\nu}_x = 870$ cm^{-1}. This value corresponds well with that found for saturated ketones [12].

As a conclusion from the analysis given above, the CD. and UV. spectra of the a, β unsaturated ketone 5 are built up by two progressions:

Series	CD.	Degree of polarization
(I) $\tilde{\nu}_{00} + m \cdot 1170$	positive	positive
(II) $\tilde{\nu}_{00} + 870 + m \cdot 1170$	negative	negative

If the very small CD. band at 26,380 cm^{-1} in the isotropic solution is connected with the 0,0-transition, one would have to assume that the sign of the CD. can change within a progression. For this there exists no hint at the moment. This band can also be a consequence of the superposition of the first negative CD. band of $\Delta\varepsilon_{11}^A(\tilde{\nu}) + \Delta\varepsilon_{22}^A(\tilde{\nu})$ and the first positive band of $\Delta c_{33}^A(\tilde{\nu})$ as a function of ρ. If one follows the line connecting the maxima of the first band as a function of ρ in *Figure 7*, one comes straightforward to the position where this small positive CD. band is found.

In the isotropic solution the series II prevails against I. By orientation and a measurement of the CD. along the optical axis, the intensity of the positive series I outweighs the intensity of the second series (II) and therefore the CD. band will be more and more positive if the order increases. This is shown schematically in construction of the experimental curves in *Figure 10e* $\left(\Delta\varepsilon_{\mathrm{iso}}(\tilde{\nu})\right)$, *Figure 10f* $\left(\Delta\varepsilon^A(\tilde{\nu})\right)$ and *Figure 7*.

REFERENCES

[1] *H.-G. Kuball, T. Karstens & A. Schönhofer*, Chem. Physics *12*, 1 (1976).
[2] a) 'Liquid Crystals', *S. Chandrasekhar*, Cambridge University Press 1977;
    b) 'Introduction to Liquid Crystals', Ed. E.B. Priestley, P.J. Wojtowicz, P. Sheng, Plenum Press New York, London 1975.
[3] To be published.
[4] Part III of this series: to be published.
[5] E.g.*P. Diehl & C.L. Khetrapal*, Mol. Physics *14*, 283 (1967).
[6] *H. Bässler & M.M. Labes*, Phys. Rev. Letters *21*, 1791 (1968); J. chem. Physics *51*, 1846, 3213 (1969); *E. Sackmann, S. Meiboom, L.C. Snyder, A.E. Meixner & R.E. Dietz*, J. Amer. chem. Soc. *90*, 3567 (1968); *W. Haas & J. Adams*, J. electrochem. Soc. *118*, 1372 (1970); *S. Sato & M. Wada*, Japan J. appl. Physics *11*, 1566 (1972).
[7] 'Application of Liquid Crystals', *G. Meier, E. Sackmann & J.G. Grabmaier*, Springer Verlag Berlin, Heidelberg, New York 1975.
[8] *G. Snatzke & F. Snatzke* in 'Fundamental aspects and recent developments in optical Rotatory Dispersion and Circular Dichroism', Ed. F. Ciardelli, P. Salvadori, Heyden & Son Ltd. 1977, page 109.
[9] *R. Weiland*, Diplomarbeit Universität Kaiserslautern 1977.
[10] *R. Kulbach*, Dissertation, Universität Kaiserslautern 1978; *H.-G. Kuball & T. Karstens*, Angew. Chem. *87*, 200 (1975); international Ed. *14*, 176 (1975).
[11] *M. Acimis*, Dissertation, Universität Kaiserslautern 1976.
[12] *O.E. Weigang jr.*, J. chem. Physics *43*, 3609 (1965).