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Structure and Function of Biopolymers: Experimental and Theoretical Techniques.

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CD polarized spectroscopy and ACD spectroscopy

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1. INTRODUCTION

1.1. CHIRAL MOLECULES AND CHIRAL CONFORMERS

Describing molecules, at first, the connectivity of the atoms in a molecule should be given in order to determine the „constitution" of the molecules [1]. For the two compounds of composition C_2H_4ClF the following graphical formulas should be discussed:

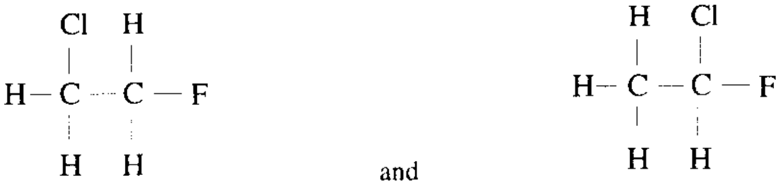

Fig. 1. Two constitutional isomers of the composition C_2H_4ClF.

Fig. 1 is a two-dimensional graph in which the atoms are linked to each other by a bond. Because in reality molecules are three dimensional structures, the configuration has to be known. Using the examples of fig. 1, there follows, e.g.:

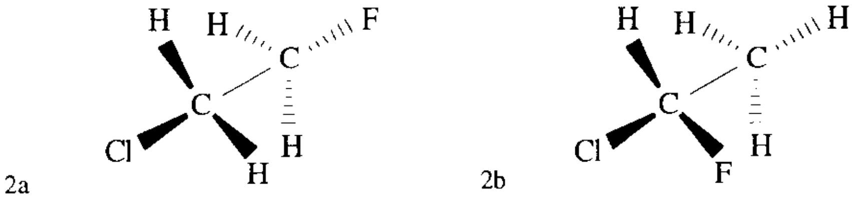

Fig. 2: The configurations of molecules of the composition C_2H_4ClF.

Because of the flexibility of the molecules through the variation of internal coordinates, e.g. rotation around the single bond betweeen two carbon atoms C - C, the molecules possess different conformations. For the molecule of fig. 2a then two forms may exist:

Fig. 3a.

These forms can also be given by a Newman projection as shown in fig 3b. These two forms are called „conformational isomers" or „conformers" of a molecule of composition C_2H_4ClF. At this point of discussion it is unimportant to discuss whether these molecules are stable species or not because only the structural aspect should be analyzed here. There is a possibility to classify molecules by using their symmetry. The following symmetry elements (symmetry operations) have to be used:

identity I

rotation axis C_n
(equivalent situation by a rotation about $\alpha = 360/n$)
rotation reflection axis S_n
(equivalent situation by a rotation
about 360/n followed by a reflection at a plane (σ_h)
to which the C_n axis is perpendicular: $S_n = \sigma_h C_n$).

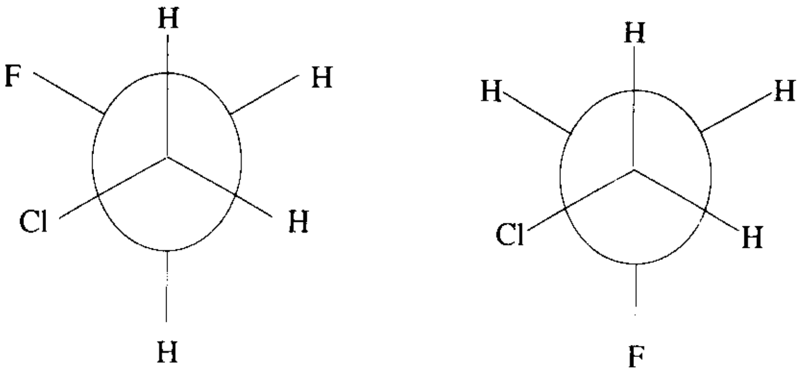

Fig. 3b.

For the compounds in the static form given in fig. 3 there are in the left conformer the symmetry elements:
I, σ (symmetry group C_s with Schoenflies nomenclature)
and in the right conformer the symmetry elements:
I (symmetry group C_1 with Schoenflies nomenclature).

In this sense all molecules and this means also all conformers of a molecules can be classified by their point symmetry group. One can find three different classes of symmetry:

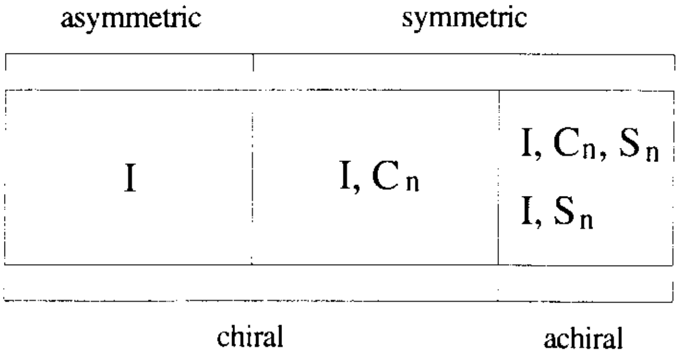

Fig. 4.

It should be pointed out here that this classification in the given form can only be done for each conformer. Molecules belonging to point symmetry group C_n, D_n, T, and O (Schoenflies nomenclature) do exist in two forms which are mirror images of each other. In the sense of Kelvin [2] they are called chiral by the following definition:

Lord Kelvin, 1884

„I call any geometrical figure or group of points *"chiral"* ,and say it has *"chirality"*, if its image in a plane mirror, ideally realized, cannot be brought[1] into coincidence with itself"

In the language of symmetry, molecules which do not have symmetry elements of the second kind, i. e. rotation reflexion axes S_n ($S_1 = \sigma$, $S_2 = i$ inversion), are chiral. The two forms have to be classified by a suitable standard nomenclature [3] in their absolute configuration given by Cahn, Ingold, Prelog (CIP) with the R, S nomenclature or in their helicity by P, M nomenclature. Chiral centers, chiral axes and chiral planes have to introduced for the description of the molecules within the scope of R, S or P, M nomenclature [3].

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[1] by rotation and translation of the geometrical figure or the group of points

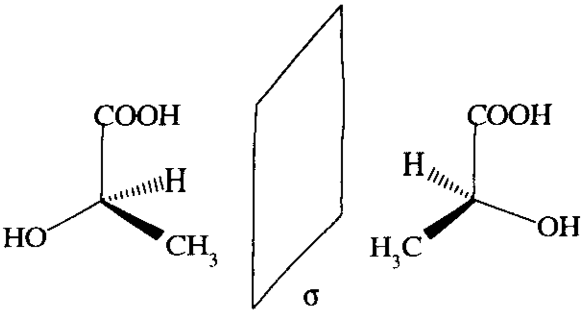

Fig. 5a.

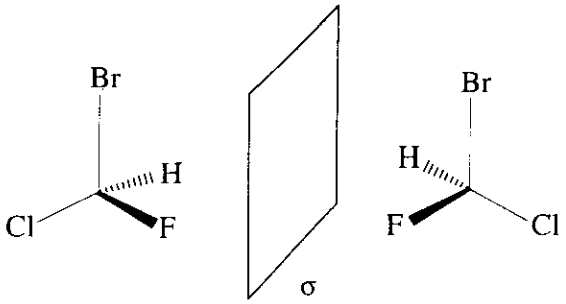

Fig. 5b.

Fig. 3 and fig. 5b, e.g. show the enantiomers of two compounds. The enantiomers in fig. 3 and fig. 5b are in each case of equal energy but there is an essential difference in the size of activation barrier between both forms. Whereas for C_2H_4ClF only a rotation about one internal coordinate (C -C-bond) is necessary for CHFCLBr one bond has to be broken and connected again in a racemization process. Because in the first case the activation energy $AE < kT$ at room temperature, both forms of C_2H_4ClF are of equal concentration in a solution or the equilibrium constant is 1. By this one could say in the language of chemistry that the compound is achiral. But it should be pointed out here that the compound of fig. 3 is achiral „in the mean“ in contrast to methane or ethane e.g. where only achiral conformers exist as long as no dynamical processes of vibrations (variation of all internal coordinates) are taken into account. But this is a process which is normally not of importance for problems in chemistry or biology.

From the discussion given above, I will finish this introduction with the statement:
For classification of the compounds with respect to fig. 5 one has to take into account each species, i. e. each conformer. By this compounds may be achiral because each species is achiral or achiral „in the mean“ because the barrier of activation between two chiral species (conformers, e.g.) is two small in order to have stable species in a thermodynamical sense. Using this concept compounds may be chiral without having an asymmetric carbon atom, e.g. as C_2HCLF which in the text books will be classified as achiral compounds. Here, in this language the system is in a state of a racemic mixture.

[1] E. L. Eliel, S. H. Wilen, Stereochemistry of Organic Compounds, John Wiley & Sons, NY, 1994.
[2] Lord Kelvin, The Baltimore Lectures on Molecular Dynamic and the Wave Theory of Light, C.J. Clay & Sons, London.
[3] R. S. Cahn, C. K. Ingold, V. Prelog, Angew. Chem. Int. Ed. **5** (1966) 385.

1.2.. DETERMINTION OF THE ABSOLUTE CONFIGURATION

The absolute configuration can be determined in an absolute sense by the Bijvoet method, i.e. determination of the phase of x-ray diffraction. This method needs „heavy“ atoms within the molecule for a good determination of the phase of the scattered light. Furthermore, from the preparative point of view, good crystals are a peremptory demand. The next point to say is that then there are only pieces of information for the solid state. In solution conformers of different structure may exist. Thus, other methods has been introduced. One of the well established method is the circular dichroism spectroscopy and a possible new one could be the chiral induction i.e. the transfer of a nematic phase to a cholesteric phase by dissolving a chiral molecule. For both methods rules are demanded which correlates the sign of the measured effect, i. e. the sign of the Cotton effect (CE) in the first or the sign of the helical twisting power (HTP) in the latter case, with the absolute configuration.

Whereas for the CD spectroscopy sector rules and helicity rules have been developed in last three decades, for the HTP no applicable rules exist at the moment. In order to develop sector and helicity rules the molecules have to be decomposed in two parts, i.e. in a chromophore and the residue of the molecules or in the sense of Snatzke in „spheres“ which are fictitious areas of the molecules which interacts with different strength. Normally the chromophore is chosen as the first sphere. The notion „chromophore“ is not easy to explain. I would like to define the chromophore as the area of a molecule which change the structure by exiting the molecule with light of a spezific wavenumber. In a different language, a chromophore is the area of a molecule which is responsible for a light absorption. A substitution of a groups connected to this area do not influence the UV spectra. Now one can ask whether the chromophore has a symmetry element of second kind (S_n) or not. In the first case one speaks about a

inherent symmetric chromophore or achiral 1.sphere

in the second case from a

inherent dissymmetric chromophore or 1.chiral sphere.

Sector rules can be developed for the first case whereas helicity rules have to be derived for the second case. Interaction of two chromophores in a molecule leads to an exciton coupling which results in a new typ of Cotton effect. By this type of interaction the absolute configuration can also be determined by the sign of the exciton couplet. This „Exciton Chirality Method“ is not within the scope of my lectures and will be discussed elsewhere.

2. CIRCULAR DICHROISM OF ORIENTED MOLECULES

Optical rotatory dispersion (ORD) and circular dichroism (CD) measurements in the visible and UV spectral regions, the Cotton effect (CE), have been used in the last three decades as an efficient method to determine the absolute configuration or conformations of molecules in solution. Because of the smaller band width of dispersion in CD as compared to that in ORD, there is a clear preference for applying CD and, accordingly, rapid developments in CD equipment have taken place. Since CD and ORD are correlated by a Kramers-Kronig transformation [1], no information is lost by this practice. ORD measurements have to be performed only when there is no absorption band in the accessible spectral region. In the CD method, the chromophores of a molecule are used as labels for the molecular chirality. Numerous papers have been published in which rules connecting the sign of the CE with the absolute configuration of the molecule have been postulated and proven [2,3,4]. In looking for new applications and developments in CD spectroscopy during the last decades, many items have to be mentioned. Firstly the method has been expanded by the introduction of chromophores into the molecules. Organic functionalities, e.g., benzoate groups, have been used in order to introduce exciton coupling which, in turn, guarantees a large CD effect and a certain determination of the absolute configuration of the surroundings at the position of substitution [5]. In the chemistry of polyhydroxy compounds, e.g., complex formation with transition metals has been applied [6]. In this latter case, the formulation of new sector or helicity rules is in progress. Another and natural development of the CD method is the expansion of the spectral range to include the vacuum UV [7] and IR [8] regions. Raman optical activity [9] and circular polarization of fluorescence/phosphorescence [10] should also be mentioned here. If only a small amount of a compound is available, its chirality can be detected by chiral induction in a nematic phase [11]. However, this method has been found to be of only limited value because the correlation between the helicity of the emerging cholesteric phase and the absolute configuration of the inducing compound is not unambiguous [12]. Mechanisms which allow a secure prediction of this absolute configuration from the helicity of the cholesteric phase are not well-understood at the moment. Sometimes a change of the helicity of the cholesteric phase occurs when "achiral variables" such as, e.g., temperature and concentration of the solute [13], are altered.

There is another potentially powerful application of CD spectroscopy which, although it has been known for a very long time [14] and is quite different from the new developments mentioned above, has not often been utilized because of various experimental problems and its theoretical complexity [15]: the measurement of the CD of oriented molecules (ACD: CD of anisotropic samples). This can now be performed with a fair accuracy since suitable experimental techniques and theoretical descriptions have become available [16,17] turning this experiment into a standard method. Two possibilities are obvious: the first is its application as a qualitative fingerprint method [18] and the second as a quantitative analysis of molecular properties. One of the problems associated with the method is the necessity to estimate the degree of orientation of the molecules. Variations in this amount of order may change the sign of the measurable quantity $\Delta\varepsilon^A$. Furthermore, the experimental effect, i.e. $\Delta\varepsilon^{A}$ - $\Delta\varepsilon$ where $\Delta\varepsilon$ represents the isotropic CD, is small and thus a sufficiently high degree of ordering is required; however, this cannot be obtained by all of the techniques available for orienting molecules [19]. The quantitative application is restricted by a lengthy measurement process which is much more laborious than that of normal CD measurements. Another difficulty is the artifact-free measurement of $\Delta\varepsilon^{A}$. Because the artifacts from linear dichroism and birefringence were not always taken into consideration in the past the ACD method was brought into disrepute in the literature.

Furthermore, there is the problem of complexity. With ACD measurements, the samples are anisotropic, i.e. they exhibit different properties in different spatial directions. The physical properties of such molecular systems cannot be described by scalar quantities alone; vectors and tensors are also needed. For a refined analysis of the ACD it is impossible to ignore the use of tensor properties. Three tensors are of exceptional importance for ACD spectroscopy: the transition moment or the absorption tensor (D_{ij}^{NK} or ε_{ij}) [16,17], the rotation or the circular dichroism tensor (R_{ij}^{NK} or $\Delta\varepsilon_{ij}$) [16,17], and the order tensor (g_{ij33}) [20]. For each tensor there exists a coordinate system of 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 spectroscopic effects: $\overset{+}{x}_i$ for D_{ij}^{NK} or ε_{ij}, $\overset{\circ}{x}_i$ for R_{ij}^{NK} or $\Delta\varepsilon_{ij}$, and $\overset{*}{x}_i$ for g_{ij33}. The molecule-fixed x_i coordinate system to which the above-mentioned tensor coordinates refer is arbitrary.

3.1. THE ACD METHOD

3.1.1. The molecular information

From the theoretical point of view the result $\Delta\varepsilon$ of the CD measurement of an isotropic solution is the sum of three quantities $\Delta\varepsilon_{ii}$:

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

The $\Delta\varepsilon_{ii}$ ($i = 1,2,3$) values are new possible sources of information. They may help to analyze the failure of helicity rules [16] since, on going from one enantiomer or local enantiomer to the other, not only $\Delta\varepsilon$ but also each $\Delta\varepsilon_{ii}$ term 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 $\sum_{i}\Delta\varepsilon_{ii}^{\mu m} = 3\Delta\varepsilon$. The other sources of chirality information, $\Delta\varepsilon_{ii}^{\mu m}$ and $\Delta\varepsilon_{ii}^{\mu Q}$, are only measurable in an anisotropic medium; the $\Delta\varepsilon_{ii}^{\mu Q}$ terms cancel in an isotropic solution. A knowledge of the coordinates $\Delta\varepsilon_{ii}$, $\Delta\varepsilon_{ii}^{\mu m}$, and $\Delta\varepsilon_{ii}^{\mu Q}$ may open a new field to obtain structural information by means of novel sector rules for these quantities.

Analogously to eq. (1), the molar decadic absorption coefficient is also the sum of three quantities ε_{ii} :

$$\varepsilon = \frac{1}{3}(\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33}). \tag{2}$$

$\Delta\varepsilon_{ii}$ and ε_{ii} ($i = 1,2,3$) are a CD and an absorption coefficient measured with a light beam propagating parallel to a molecule-fixed x_i coordinate axis and a ligth beam being polarized parallel to the x_i axis, respectively. The quantity $\Delta\varepsilon_{ii}$ can be visualized according to fig. 1 by looking at the molecule in question as a part of an ensemble of molecules which are oriented parallel to each other. For the decomposition of the elliptical birefringence and dichroism into linear and circular effects, i.e. in order to obtain only chirality information [21], a mean value of at least three measurements for each $\Delta\varepsilon_{ii}$ has to be taken; for this purpose the sample is rotated about the direction of light propagation into three different positions differing by 120°. Alternatively, one can measure $\Delta\varepsilon_{ii}$ for an ensemble of molecules possessing an orientational distribution of at least C_3 symmetry about the molecule-fixed x_i axis which is parallel to the propagation direction. In order to obtain the three quantities $\Delta\varepsilon_{ii}$, these measurements have to be done for three mutually perpendicular directions of the light propagation. Analogously, the ε_{ii} quantities are measured as absorption coefficients for a completely oriented ensemble of molecules with light beams polarized parallel to the x_i directions. It should be kept in mind that for $\Delta\varepsilon_{ii}$ the index i indicates the propagation direction of light whereas for ε_{ii} it gives the polarization direction.

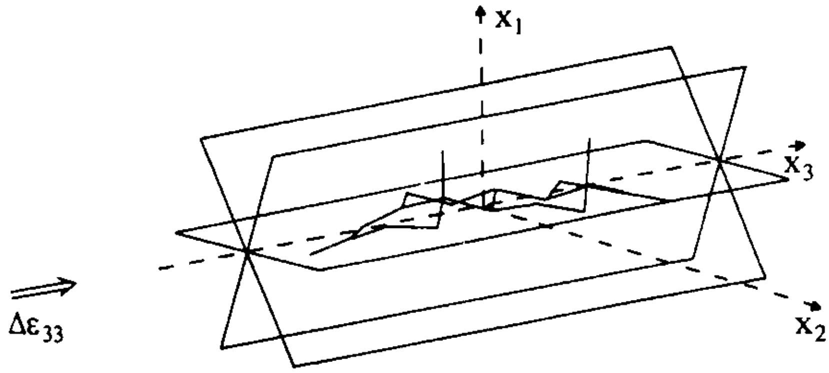

Figure 1. Experimental situation for the measurement of $\Delta\varepsilon_{33}$. The coordinates $\Delta\varepsilon_{11}$ and $\Delta\varepsilon_{22}$ are obtained analogously.

3.1.2. Experimental

A large number of techniques exists for orienting molecules [19]. ACD spectra of polymers or biopolymers can be obtained while achieving the orientation by means of a strong electric field [22] or by performing the measurements in streaming solutions [23]. Smaller molecules can be oriented by dissolving them in a liquid crystal phase (LC; guest/host system) which, in turn, is ordered by application of an electric ac or dc field [24]. Other orienting techniques have not been successful for ACD measurements to date. For measuring the ACD, the UV, and the polarized UV spectra in an LC phase, the compounds have to be dissolved to a maximum concentration of 3 - 5% by weight. Two different phases, i.e. ZLI 1695 (Merck, Darmstadt, mixture of four 4-n-alkyl-4-cyanobicyclohexanes) and the compensated nematic phase of the mixture of cholesteryl chloride and cholesteryl laurate (CC/CL; about 1.8 : 1 by weight), have been used with success. The sample thickness can be chosen between 50 µm and 2 mm; the extinction of the sample should not exceed 1 - 1.2. Higher concentrations destroy the liquid crystal matrix or enhance the depolarization of light to such an extent that ACD measurements are no longer possible. The sample thickness is also limited by the effect of depolarization which is different for different LC phases. In cases of chiral induction the phases are cholesteric after dissolution of the chiral molecules. Therefore, the phase has to be converted back to the nematic state. Otherwise, only properties determined by the helicity of the phase and not the actual molecular properties will be measured. For the measurements performed by the present authors, the sample was filled into a special cuvette [25] where the chiral induction is compensated by an electric ac field (10^6 V/m) or, for CC/CL, by variation of the temperature of the sample in addition to the applied electric field. There are techniques available to check the state of the phase if necessary [26]. The special cuvette also minimizes the linear birefringence and dichroism introduced by surface defects (disclinations) originating from the filling. In addition, the windows of the cuvette are coated in order to provide a good homeotropic orientation at the surface [27]. The sample was adjusted in a commercial CD spectrometer. For the ACD measurements, the optical axis of the uniaxial nematic 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 performed 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 of the substance because of the long measuring times, at first $\Delta\varepsilon$ (T = 80 °C), then $\Delta\varepsilon^A$ (six times for each temperature), and then again $\Delta\varepsilon$ (T = 80 °C) were measured. The degree of anisotropy R was determined by polarized spectroscopy using a UV spectrometer equipped with a polarizing prism [20]. The amount of order can be determined also by NMR, especially by the ^{2}H NMR spectra [28]. To control the temperature of the probes for the different measurements (ACD, NMR, etc.), the temperature units were calibrated with a Pt 100 resistor.

3.2. DESCRIPTION OF POLARIZED SPECTROSCOPY

3.2.1. The order parameters

The optical properties of anisotropic samples depend on the orientational order of the molecules which can be measured by the absorption of polarized light or can be determined by NMR spectroscopy. For the present purpose, the orientational order can be described by the orientational distribution coefficients

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

a_{ij} is the transformation matrix from the space-fixed x_i' to the molecule-fixed x_i coordinate system. $f(\alpha,\beta,\gamma)$ is the orientational distribution function and α,β,γ are the Eulerian angles as defined in ref. [29]. For uniaxial systems as assumed here, the order parameters S* and D* may be introduced instead of the g_{ij33} :

$$S^* = (3g^*_{3333} - 1)/2, \qquad (4)$$

$$D^* = \sqrt{3}(g^*_{2233} - g^*_{1133})/2. \qquad (5)$$

They refer to the optical axis of the macroscopic sample which is chosen as the space-fixed x_3' axis and to the molecule-fixed x_i^* coordinate system. These principal axes of g_{ij33} are fixed by symmetry for molecules with a point symmetry group different from C_1, C_2, C_i, C_s, and C_{2h} [20]. In the cases of the latter point groups the orientations of the x_i^* axes with respect to the molecular skeleton have to be determined experimentally (determination of all elements of g_{ij33}); the orientations of the x_i^* axes vary, in general, with temperature. The two order parameters S* and D* can be measured - albeit with the use of some approximations - by IR, VIS, UV, or NMR spectroscopy or by other techniques [30]. Whereas S* characterizes the order of the orientation of the molecule-fixed x_3^* axis with respect to the optical axis of the uniaxial phase, the parameter D* is a measure for the deviation from a rotationally symmetrical distribution of the molecules about their x_3^* axis.

3.2.2. The polarized absorption

The molar decadic absorption coefficient for light polarized parallel (ε_1) and perpendicular (ε_2) to the optical axis of a uniaxial sample is given by

$$\varepsilon_k = \sum_{i,j} g_{ijkk}\varepsilon_{ij} = \sum_{i,j} a_{ij}^2 g^*_{jjkk}\varepsilon^+_{ii} \quad (k = 1,2). \qquad (6)$$

ε_{ii}^{+} are the absorption coefficients for light beams polarized linearly parallel to the x_i^{+} axes (principal axes of ε_{ij}) in a completely oriented system. The a_{ij} in eq. (6) are here the elements of the matrix which transform the x_i^{*} coordinates into the x_i^{+} coordinates. The ε_{ii}^{+} terms are related to the absorption coefficient of the isotropic solution by

$$\varepsilon = \frac{1}{3}(\varepsilon_1 + 2\varepsilon_2) = \frac{1}{3}(\varepsilon_{11}^{+} + \varepsilon_{22}^{+} + \varepsilon_{33}^{+}). \tag{7}$$

If there is no temperature dependence of the x_i^{*} axes, an appropriate description of the anisotropic absorption is given by

$$\varepsilon_1 - \varepsilon = (\varepsilon_{33}^{*} - \varepsilon)S^{*} + \frac{1}{\sqrt{3}}(\varepsilon_{22}^{*} - \varepsilon_{11}^{*})D^{*}. \tag{8}$$

Otherwise, the ε_{ii}^{*} terms refer to different x_i^{*} axes for different temperatures. Furthermore, from eq. (6) it follows for the degree of anisotropy that

$$R = \frac{\varepsilon_1 - \varepsilon_2}{3\varepsilon} = \frac{1}{2}\sum_{i,j}(3g_{ij33} - \delta_{ij})q_{ij}; \quad q_{ij} = \frac{\varepsilon_{ij}}{3\varepsilon}. \tag{9}$$

If the molecule-fixed coordinate system is arbitrarily chosen, non-diagonal elements occur in eq. (9).

3.2.3. ^{2}H NMR spectroscopy

If only the polarized spectroscopy is applicable to the class of molecules under consideration, there is no possibility for a complete analysis. In order to obtain the maximum amount of information from the ACD and the polarized UV absorption, all elements of the order tensor g_{ij33} should be known; these can, in principle, be determined from the nuclear quadrupole coupling in the ^{2}H NMR spectra. From equations given by Veracini [28] for the splitting of the ^{2}H NMR signal of one C-D bond, it follows, written in our notation, that

$$\Delta\nu = k\sum_{i,j} g_{ij33}\xi_{ij} \tag{10}$$

where ξ_{ij} is the nuclear quadrupole tensor. For a host system with an anisotropy of the magnetic susceptibility $\Delta\chi > 0$ or $\Delta\chi < 0$, $k = 3/2$ or $k = -(3/4)$, respectively, and g_{ij33} refers in each case to the director of a locally nematic phase. To determine all elements g_{ij33}, the signals of five different C-D bonds within the molecule are necessary. Here certain situations must be excluded. For instance, no more than three bond directions - not two, as erroneously mentioned in [31] - may lie in the same plane or, more generally, possess a common normal, no bond direction may be perpendicular to three others, and no three directions may be mutually perpendicular. For the evaluation their splitting values $\Delta\nu$ are measured as functions of the temperature. The diagonal and rotationally symmetrical nuclear quadrupole tensors ξ'_{ij} which refer to the five bond directions (ξ'_{33} = 185 kHz for an sp^2- and 170 kHz for an sp^3-bond; $\eta = 0$ [28]) are transformed to the x_i coordinate system. With the resulting five tensors ξ_{ij}, eq. (10) yields a system of five linear equations from which all independent coordinates g_{ij33} can be obtained [31]. By diagonalization of the order tensor, it is possible to derive the order parameters S*, D*, and the orientation of its principal axes 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 ε_{ij} and $\Delta\varepsilon_{ij}$ can be estimated if the eigenvalues g_{ii33}^{*} and the orientation of the x_i^{*} axes depend on the temperature.

3.2.2. The ACD spectra

For the ACD of low symmetry molecules where the orientation of the principal axes of the order tensor g_{ij33} relative to the molecular frame is temperature-dependent, one may use the formula:

$$\Delta\varepsilon^{A} = \sum_{i,j} g_{ij33}\Delta\varepsilon_{ij} = \sum_{i,j} a_{ij}^{2} g^{*}_{jj33}\Delta\varepsilon^{\circ}_{ii}. \qquad (11)$$

The light beam is assumed here to propagate parallel to the optical axis (x'_3). The eigenvalues $\Delta\varepsilon^{\circ}_{ii}$ describe the molecular property $\Delta\varepsilon_{ij}$ in its system of principal axes (x°_i). They are related to the CD of the isotropic solution by eq. (1). The terms a_{ij} are the elements of the matrix which transforms the x^{*}_i coordinates into the x°_i coordinates. For $\Delta\varepsilon^{A}$ and the ACD $\Delta\varepsilon^{A}_{2}$ for light propagating perpendicular to the optical axis the following relation is valid:

$$\Delta\varepsilon = \frac{1}{3}(\Delta\varepsilon^{A} + 2\Delta\varepsilon^{A}_{2}). \qquad (12)$$

Because of the interference with linear birefringence and dichroism, the present authors have not yet been able to measure $\Delta\varepsilon^{A}_{2}$ for liquid crystal guest/host systems. If the temperature dependence of the orientation of the x^{*}_i axes is neglected, $\Delta\varepsilon^{A}$ can be conveniently described by

$$\Delta\varepsilon^{A} - \Delta\varepsilon = (\Delta\varepsilon^{*}_{33} - \Delta\varepsilon)S^{*} + \frac{1}{\sqrt{3}}(\Delta\varepsilon^{*}_{22} - \Delta\varepsilon^{*}_{11})D^{*}. \qquad (13)$$

This formula is analogous to eq. (8).

The $\Delta\varepsilon_{ij}$ term can be decomposed into an electric dipole/magnetic dipole and an electric dipole/electric quadrupole contribution:

$$\Delta\varepsilon_{ij}(\bar{v}) = \Delta\varepsilon^{\mu m}_{ij}(\bar{v}) + \Delta\varepsilon^{\mu Q}_{ij}(\bar{v}). \qquad (14)$$

In general, the decomposition is origin-dependent. From the diagonal elements $\Delta\varepsilon_{ii}$, the quantities $\Delta_i(\bar{v})$ defined by

$$\Delta_1(\bar{v}) = \frac{1}{2}\left[\Delta\varepsilon_{11}(\bar{v}) - \Delta\varepsilon_{22}(\bar{v}) - \Delta\varepsilon_{33}(\bar{v})\right] \qquad (15)$$

and cyclic permutation of the indices 1, 2, 3 can be calculated. The $\Delta_i(\bar{v})$ terms yield information about the electric dipole $(\langle\mu_i\rangle_{on})$, magnetic dipole $(\langle m_i\rangle_{no})$, and electric quadrupole $(\langle Q_{ij}\rangle_{no})$ transition moments for a transition between two different vibronic-electronic states $|0\rangle \rightarrow |n\rangle$ with the spectral function $G^{on}_{(\bar{v})}$:

$$\Delta_i(\bar{v}) = -\frac{1}{2}B\bar{v}\sum_{n}\mathrm{Im}\{\langle\mu_i\rangle_{on}\langle m_i\rangle_{no}\}G^{on}_{(\bar{v})} + \Delta\varepsilon^{\mu Q}_{ii}(\bar{v}). \qquad (16)$$

In order to eliminate the frequency dependence, one may calculate the anisotropic rotational strength R^A for the electronic transition $|N\rangle \rightarrow |K\rangle$ [16,17]

$$R^A = \frac{3}{B}\int \frac{\Delta\varepsilon^A(\bar{\nu})}{\bar{\nu}}d\bar{\nu} = 3\sum_{i,j} g_{ij33}R_{ij}^{NK}; \quad \frac{3}{B} = 22.96\cdot 10^{-40}\ (\mathrm{cgs}). \tag{17}$$

For an isotropic solution, $g_{ij33} = \frac{1}{3}\delta_{ij}$, and R^A becomes the rotational strength:

$$R^{NK} = \sum_i R_{ii}^{NK} = \frac{3}{B}\int \frac{\Delta\varepsilon(\bar{\nu})}{\bar{\nu}}d\bar{\nu} \tag{18a}$$

where

$$R_{ij}^{NK} = \frac{1}{B}\int \frac{\Delta\varepsilon_{ij}(\bar{\nu})}{\bar{\nu}}d\bar{\nu} \tag{18b}$$

is the tensor of rotation. The decomposition of R_{ii}^{NK} corresponding to eq. (14) yields

$$R_{11}^{\mu m} = \mathrm{Im}\left\{\langle\mu_2\rangle_{NK}\langle m_2\rangle_{KN} + \langle\mu_3\rangle_{NK}\langle m_3\rangle_{KN}\right\}, \tag{19}$$

$$R_{11}^{\mu Q} = -\langle\mu_2\rangle_{NK}\langle Q_{31}\rangle_{KN} + \langle\mu_3\rangle_{NK}\langle Q_{21}\rangle_{NK}. \tag{20}$$

R_{22}^{NK} and R_{33}^{NK} are derived by cyclic permutation of the indices. The terms $<\mu_i>_{NK}$, $<m_i>_{KN}$, and $<Q_{ij}>_{KN}$ are the electric dipole, magnetic dipole, and electric quadrupole transition moments for the electronic transition $|N\rangle \rightarrow |K\rangle$. By integration of eqs. (15) and (16), wavenumber-independent quantities Δ_i can be obtained with the tensors of rotation given by eqs. (19) and (20):

$$\Delta_1 = \frac{1}{2}\left[R_{11}^{NK} - R_{22}^{NK} - R_{33}^{NK}\right] \tag{21}$$

and cyclic permutation of the indices 1, 2, 3. The following analogue of eq. (16) is then valid:

$$\Delta_i = -\frac{1}{2}\mathrm{Im}\left\{\langle\mu_i\rangle_{NK}\langle m_i\rangle_{KN}\right\} + R_{ii}^{\mu Q}. \tag{22}$$

3.3. RESULTS AND DISCUSSION

3.3.1. Reliability of ACD measurements

No discussion of ACD measurements may start without an assessment of the reliability of the experimental data. These measurements can be falsified by interference from the effects of linear birefringence and dichroism. There are a number of reasons for the mixing of the signals from the linear and the circular effects in spite of the fact that both signals are different by symmetry and therefore should be mutually exclusive [32, 33]. The resulting error is difficult to estimate. However, it should always be borne in mind that the linear effect is larger by three orders of magnitude than the circular effect. One may differentiate between both effects by their dispersion properties: the dispersion curves of the optical rotation and the ellipticity of the emerging light are opposite in their form for the linear and circular effects [29]. Whether this provides a suitable method for an experimental control of the reliability of the data is not yet known. Another possibility is to measure the ACD and the AORD of a compound in an anisotropic system as a function of temperature; this has been done for testosterone propionate in CC/CL as the solvent (figs.2,3). Comparison of the results by the Kramers-Kronig transformation yields an agreement of up to 5 - 10% as shown in figs. 4, 5 [34]. Since the Kramers-

Kronig transformation applies to the linear as well as to the circular effects [29], the errors may also be transformed from one experiment to the other. For a check of the data, this can be avoided when the ACD and the AORD measurements are each of a different type; i.e., the ACD is determined by a differential absorption modulation method and not as ellipticity whereas, for the AORD, the rotation of the plane of polarization is obtained which corresponds to an ellipticity measurement.

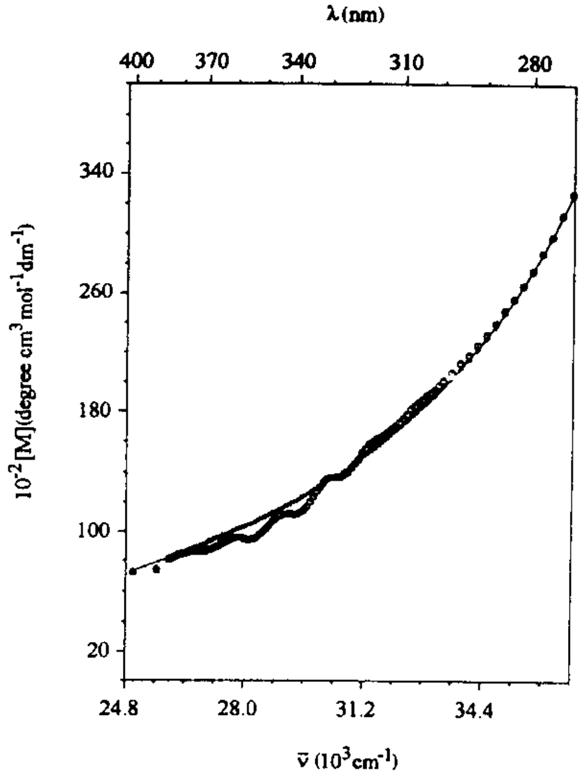

Figure 2. AORD of testosterone propionate and CC/CL: measured spectrum (O), difference curve between the experimental curve and the result of the Kramers-Kronig tranformation of fig. 3b (+). Approximated Drude term (———) [34].

3.3.2. The effect of symmetry - principal axes of $\Delta\varepsilon_{ij}$ and ε_{ij}

For complete information, the $\Delta\varepsilon^{o}_{ii}$ and ε^{+}_{ii} coordinates and the corresponding principal axes must be known. For chiral molecules with a point symmetry group C_n ($n \geq 3$) or D_n ($n \geq 2$), the x^{o}_{i}, x^{+}_{i}, and x^{*}_{i} system are fixed by symmetry. Furthermore, $D^* = 0$, $\Delta\varepsilon_{11}=\Delta\varepsilon_{22}$, and $\varepsilon_{11} = \varepsilon_{22}$ for $n \geq 3$. With $\Delta\varepsilon^A$, $\Delta\varepsilon$, R, ε, and S^*, all sources of information are then available to calculate the values of $\Delta\varepsilon^{o}_{ii}$ and ε^{+}_{ii}. Molecules of such a symmetry have not yet been investigated. Whereas, for molecules with point symmetry group C_2, one principal axis is given by the C_2 rotation axis, for molecules without any symmetry the orientations of all principal axes are unknown and have to be determined experimentally. This can be achieved if all elements of the order tensor g_{ij33} are known with sufficient accuracy as functions of temperature. A set of linear equations is then available from eqs. (11) and (6) for the determination of $\Delta\varepsilon_{ij}$ and ε_{ij}. Diagonalization yields the principal axes of both tensors. This procedure is only possible when the transformation matrices a_{ij} in eq. (11) and (6) are temperature-dependent, in other words, when the orientation of the x^{*}_{i} axes with respect to the x^{o}_{i} and x^{+}_{i} axes is temperature-dependent. Thereby the molecule or at least the region of the chromophore within the molecule must be rigid. For cholestenone, the temperature dependence of the orientation of the x^{*}_{i} axes seems to be too small for a determination of the x^{o}_{i} axes [31].

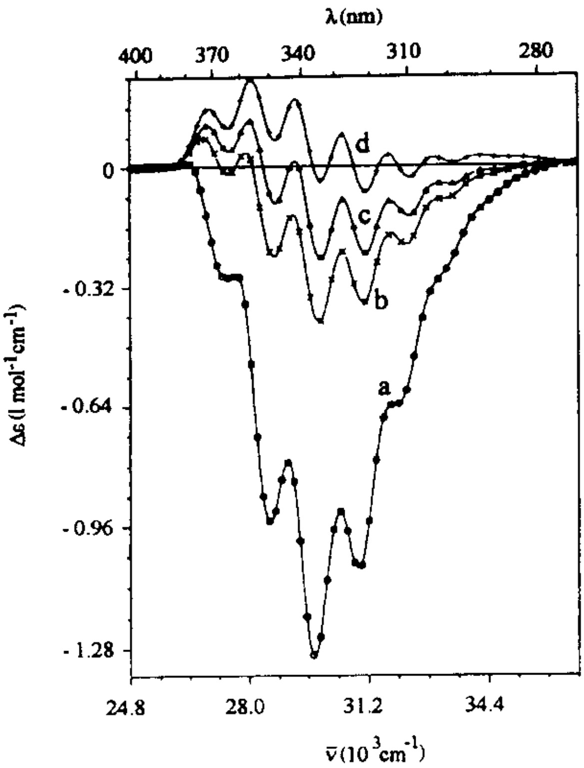

Figure 3. CD and ACD spectra of testosterone propionate in CC/Cl (1.56 : 1 for (a), (c), and (d); 1.8 : 1 for (b). From below: (a) T = 80 °C (isotropic solution), c = 0.323 mol/l; (b) T = 43 °C, c = 0.255 mol/l; (c) T = 29 °C, c = 0.324 mol/l; (d) T = 29.5 °C, c = 0.170 mol/l. The electric dc field 2.8 · 10^6 V/m for (b) and 2.0 · 10^6 V/m for (c) and (d) [34].

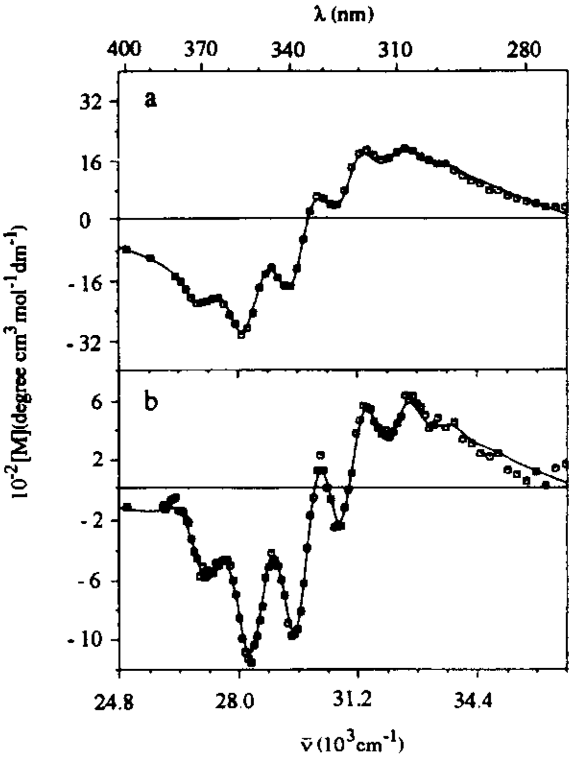

Figure 4. Experimental (□) and calculated (——) AORD curves of testosterone propionate in CC/CL; (a) corresponds to (a) and (b) to (b) in fig. 3 [34].

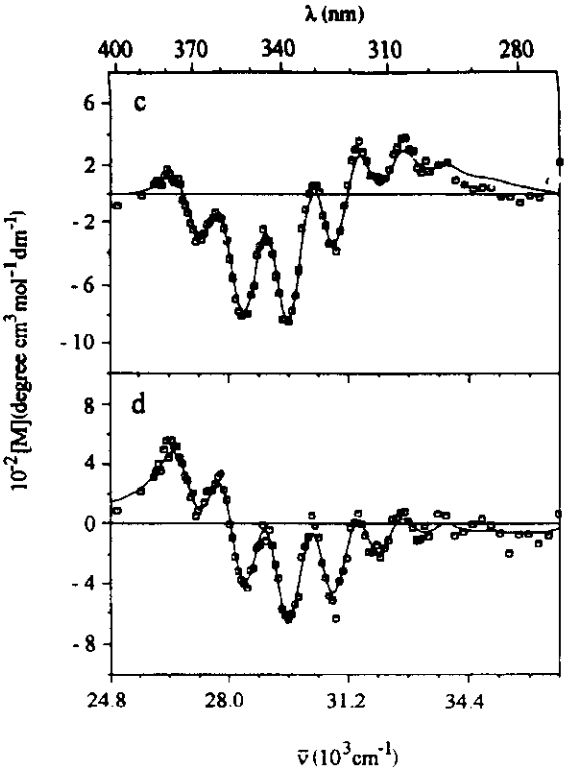

Figure 5. Experimental (□) and calculated (——) AORD curves of testosterone propionate in CC/CL; (c) corresponds to (c) and (d) to (d) in fig. 3 [34].

3.3.3. The problem of local enantiomers

On going from one enantiomer to the other by inversion at the origin of the molecule-fixed coordinate system, $\Delta\varepsilon_{ij}$ is changed into - $\Delta\varepsilon_{ij}$ and thus also $\Delta\varepsilon$ changes into - $\Delta\varepsilon$. From the experimental point of view this means that, for two enantiomers, not only $\Delta\varepsilon$ but also $\Delta\varepsilon^A$ and $\Delta\varepsilon_{ij}$ are equal in size but different in sign when measured under the same conditions. Conversely, one might conclude from an experiment where $\Delta\varepsilon$ and -$\Delta\varepsilon$ have been found for two compounds that these compounds are enantiomers. Because the agreement for $\Delta\varepsilon$ could be fortuitous, measurements of $\Delta\varepsilon^A$ and a $\Delta\varepsilon_{ij}$ would corroborate this assumption. This type of application of the ACD spectroscopy seems to be trivial. A more complex situation evolves when, for one and the same compound, a change of sign of $\Delta\varepsilon$, occurs, e.g. when going from one solvent to another, whereas $|\Delta\varepsilon|$ remains approximately the same. Then again the question arises whether the molecule has adopted a conformation in which the chromophore and its surroundings are approximately in an enantiomeric form, e.g., the dihedral angle ϕ between two bonds of a chromophore has changed to -ϕ, approximately. In such a situation the expressions "local enantiomers" or sometimes "quasi-enantiomers" are often used in the literature. ACD spectroscopy could be able to differentiate locally enantiomeric forms where the $\Delta\varepsilon_{ij}$ should be different in sign and similar in their absolute values from very different structures where an accidental compensation of very different $\Delta\varepsilon_{ij}$ terms according to eq. (1) is responsible for the behaviour of $\Delta\varepsilon$. This consideration can be transferred to molecules with similar structures, i.e. to molecules which are comparable by sector or helicity rules. The above-mentioned solvent effect is replaced here by the effect of substitution near a chromophore which itself remains unaltered so that its absorption spectrum is not changed. A change of sign of $\Delta\varepsilon$ as a consequence of such a substitution occurs, e.g., in the $n\pi^*$ transition of 2β-methylcholest-4-en-3-one in comparison to those of 2α-methylcholest-4-en-3-one or cholest-4-en-3-one. Locally enantiomeric forms of the enone chromophore may be the reason for this as has been concluded from the helicity rule for this chromophore [36]. The ACD method can be used to analyze this problem further [16]. If the above interpretation is correct, each tensor coordinate $\Delta\varepsilon_{ij}$ should also change its sign. The reduced CD spectra of cholest-4-en-3-one are shown in fig. 6. These spectra of the enone chromophore are built up from at least two contributions resulting from two different vibrational progressions I $\left(\bar{\nu} = \bar{\nu}_{00} + n\bar{\nu}_1\right)$ and II

$\left(\bar{\nu}=\bar{\nu}_{00}+\bar{\nu}_x+n\bar{\nu}_l\right)$[1] [16, 31]. The contribution $\Delta\varepsilon^*_{33} > 0$ stems from I whereas the main contribution $\Delta\varepsilon^*_{11}+\Delta\varepsilon^*_{22} < 0$ is caused by II. The two contributions (fig. 7a) yield $\Delta\varepsilon < 0$ as shown in fig. 7b. Substitution of a methyl group in the 2β- but not in the 2α-position leads to a $\Delta\varepsilon > 0$. This has been interpreted as a transition to a local enantiomer [35]. However, since the corresponding change of sign with $\Delta\varepsilon^*_{33} > 0$ and $\Delta\varepsilon^*_{11}+\Delta\varepsilon^*_{22} < 0$ cannot be found experimentally, another explanation is necessary. If the substitution would alter the contributions from both vibrational progressions to $\Delta\varepsilon^*_{33}$ and $\Delta\varepsilon^*_{11}+\Delta\varepsilon^*_{22}$ according to fig. 6, the sum would change to such an amount that a bisignated (fig. 7c) or even a positive (fig. 7d) CD curve would result. Thus, a change of sign of $\Delta\varepsilon$ according to fig. 7 might occur without going to the local enantiomer, but rather only as a result of a variation of the amount of vibronic coupling. This represents a breakdown of the helicity rule for the nπ* transition of the enone chromophore, as has been discussed in ref. [16].

Footnote: [1] $\bar{\nu}$ is the wavenumber of the maximum of the vibrational band, $\bar{\nu}_{00}$ that of the 0-0-transition, and $\bar{\nu}_x$ and $\bar{\nu}_l$ are those of a non-totally and a totally symmetrical normal vibration, respectively; n = 0, 1, 2, ...

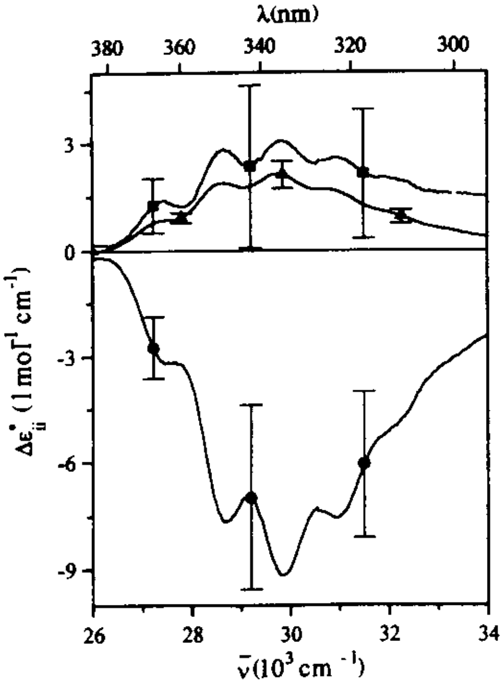

Figure 6. $\Delta\varepsilon^*_{11}$ (■), $\Delta\varepsilon^*_{22}$ (●), and $\Delta\varepsilon^*_{33}$ (Δ) of the nπ* transition of cholest-4-en-3-one in ZLI 1695. The error of the sum $\Delta\varepsilon^*_{11}+\Delta\varepsilon^*_{22}$ is comparable to that of $\Delta\varepsilon^*_{33}$ [31].

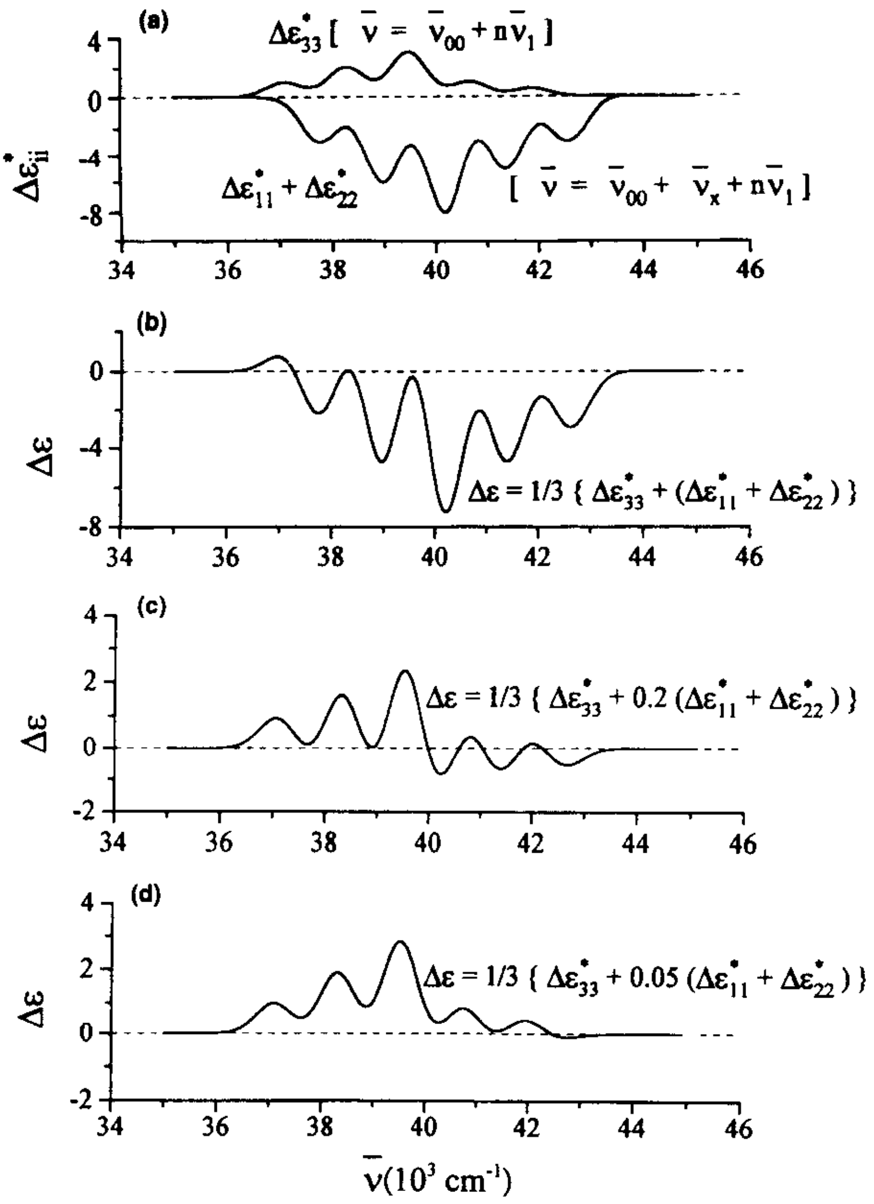

Figure 7. Superposition of a constant positive $\Delta\varepsilon^*_{33}$ and a negative $\Delta\varepsilon^*_{11} + \Delta\varepsilon^*_{22}$ decreased by substitution in the vicinity of the chromophore ($\Delta\varepsilon = 1/3\{\,\Delta\varepsilon^*_{33} + \mathrm{const.}\cdot(\Delta\varepsilon^*_{11} + \Delta\varepsilon^*_{22})\}$: alteration of the sign of $\Delta\varepsilon$ without a change of the absolute configuration [16].

3.3.4. The electric dipole/electric quadrupole contribution

To evaluate the term $\Delta\varepsilon^{\mu Q}_{ii}$, one may start from the Δ_i given in eq. (16) or eq. (22). However, there is not enough experimental information available in order to decompose Δ_i into its two parts. Only in those special cases where the electric dipole transition moment is perpendicular to an x^o_i axis, is $\Delta\varepsilon^{\mu Q}_{ii}$ given by Δ_i. It is then also origin-independent in this case. As an example for such a situation, the $\Delta\varepsilon^A$, $\Delta\varepsilon$, the degree of anisotropy R, ε, $\Delta\varepsilon_{ii}$, and ε_{ii} for 1,4-bis-(R-1-phenylethylamino)-9,10-anthraquinone have been analyzed [17] and the ACD spectra and the $\Delta\varepsilon_{ii}$ values of the charge transfer transition are shown in figs. 8 and 9. From these data, the electric dipole/electric quadrupole contribution for the charge transfer transition can be estimated as shown in fig. 10; it is of the same order of magnitude as the electric dipole/magnetic dipole contribution for this compound. For the $\pi\pi^*$ transition, the $\Delta\varepsilon^{\mu Q}_{ii}$ values exceed the $\Delta\varepsilon^{\mu m}_{ii}$ values [17].

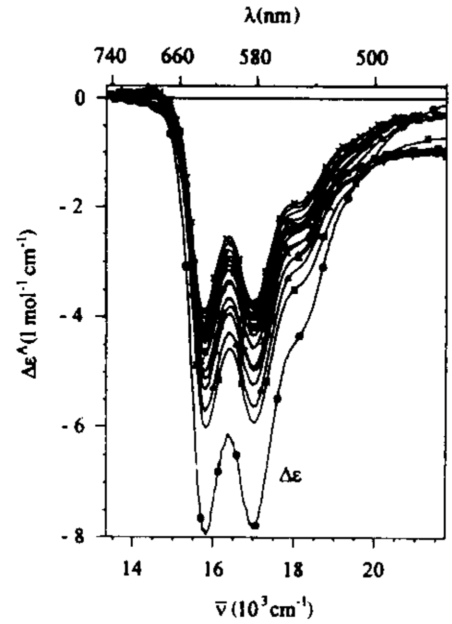

Figure 8. CD and ACD spectra of 1,4-bis-(R-1-phenylethylamino)-9,10-anthraquinone in ZLI 1695. From below: T(°C) = 80 ($\Delta\varepsilon$), 65, 62, 58, 58, 53, 48, 48, 38, 38, 33, 28, 28 ($\Delta\varepsilon^A$).

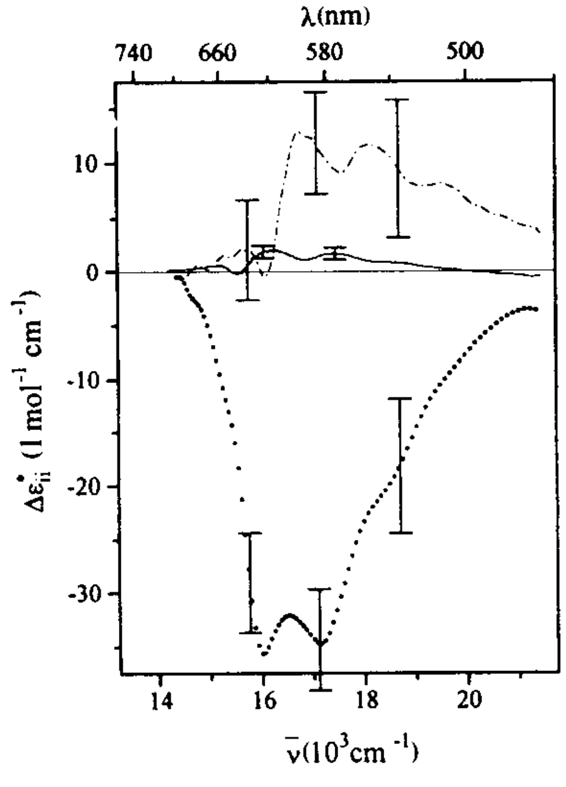

Figure 9. $\Delta\varepsilon^*_{11}$(-·-·-·), $\Delta\varepsilon^*_{22}$(·······), and $\Delta\varepsilon^*_{33}$(———) for 1,4-bis-(R-1-phenylethylamino)-9,10-anthraquinone in ZLI 1695.

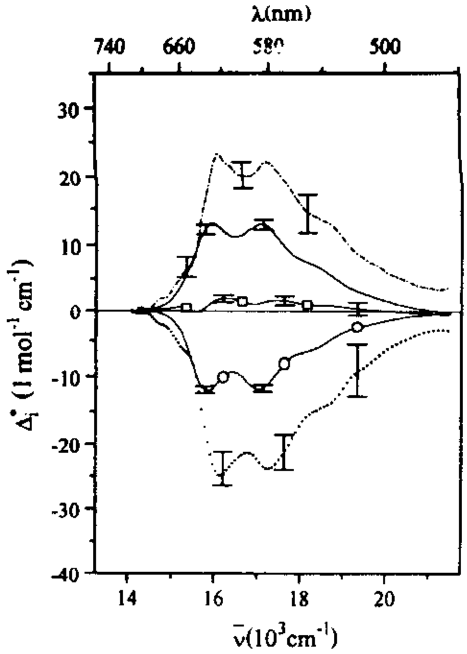

Figure 10. Δ_1^* ($\bar{\nu}$) (- - -), Δ_2^* ($\bar{\nu}$) (······), Δ_3^* ($\bar{\nu}$) (——), $\Delta\varepsilon_{33}^{\mu m}$ (○), and $\Delta\varepsilon_{33}^{\mu Q}$ (□) for 1,4-bis-(R-1-phenylethylamino)-9,10-anthraquinone in ZLI 1695.

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Fachbereich Chemie, Universität Kaiserslautern

Tuesday, 12 March 1996 9.00 - 10.00

Introduction to Circular Dichroism

Thursday, 14 March 1996 14.30 - 15.15

Phenomena Connected with the Linear and Circular Birefringence / Dichroism

Thursday, 14 March 1996 16.20 - 17.15

The Concept of Chromophores Helicity and Sector Rules with Respect to Applications (CD)

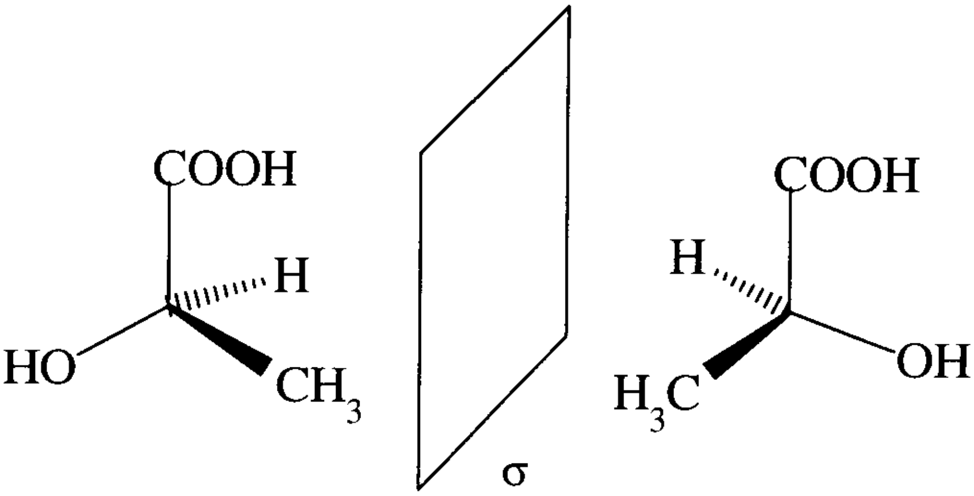
Friday, 15 March 1996 10.45 - 11.15

CD of Oriented Molecules (ACD) Introduction - Theory and Experiment

Definition der Chiralität

(Lord Kelvin , 1884)

„I call any geometrical figure or group of points *'chiral'*, and say it has *'chirality'*, if its image in a plane mirror, ideally realized, cannot be brought* into coincidence with itself"



* by rotation and translation of the geometrical figure or the group of points

Chirality

of the molecule

I	I, C_n	I, C_n, S_n I, S_n

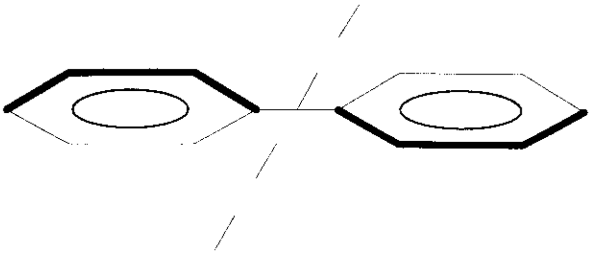
➔ rigid molecules

➔ flexible molecules

⇒ each conformer has its **own** point symmetry group

⇒ achiral systems can posses chiral conformers

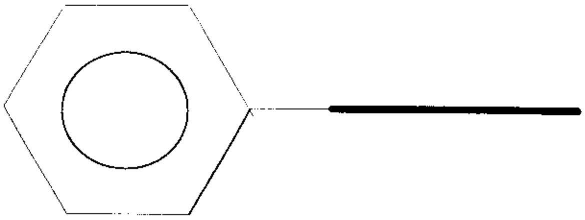
D_2



dieder angle < 90°

C_2

D_{2d}



dieder angle 90°

Chirality of molecules

Helicity of the phase

($\neg S_n$)

chiral

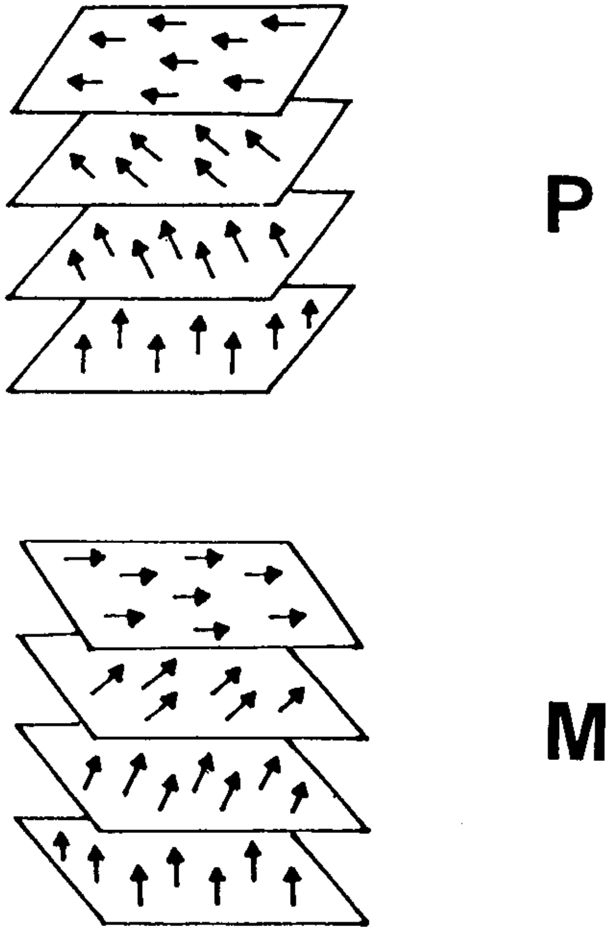
E
E, C_n

two species

R, S

?

↔

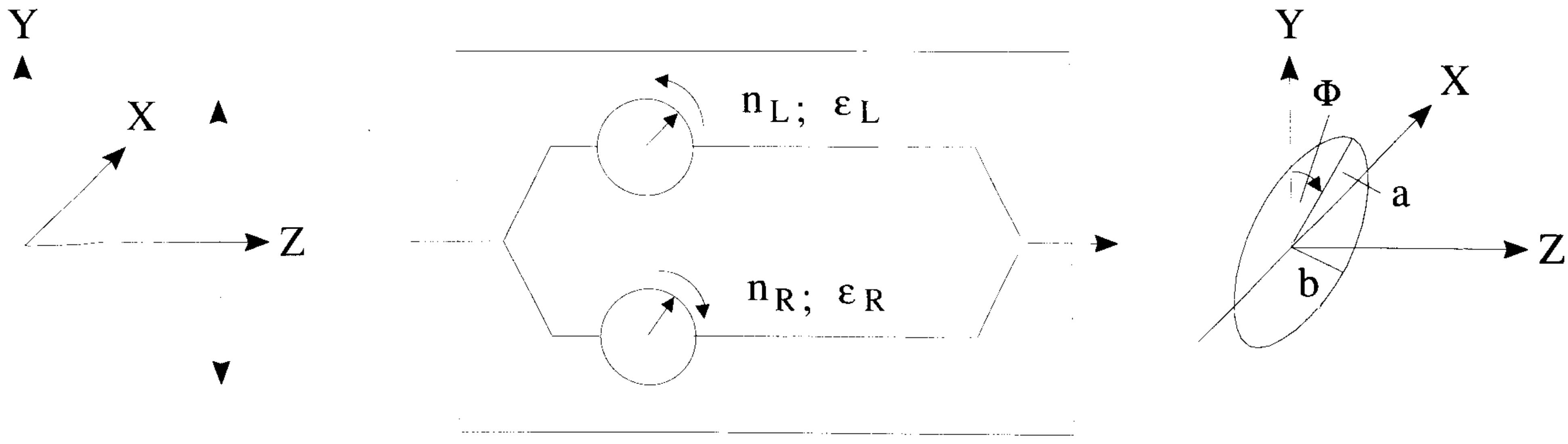


cholesteric phases

(chiral phases)

Circular Dichroism and Circular Birefringence
(Optical Activity)

Circular Dichroism Δε; Optical Rotatory Dispersion ORD

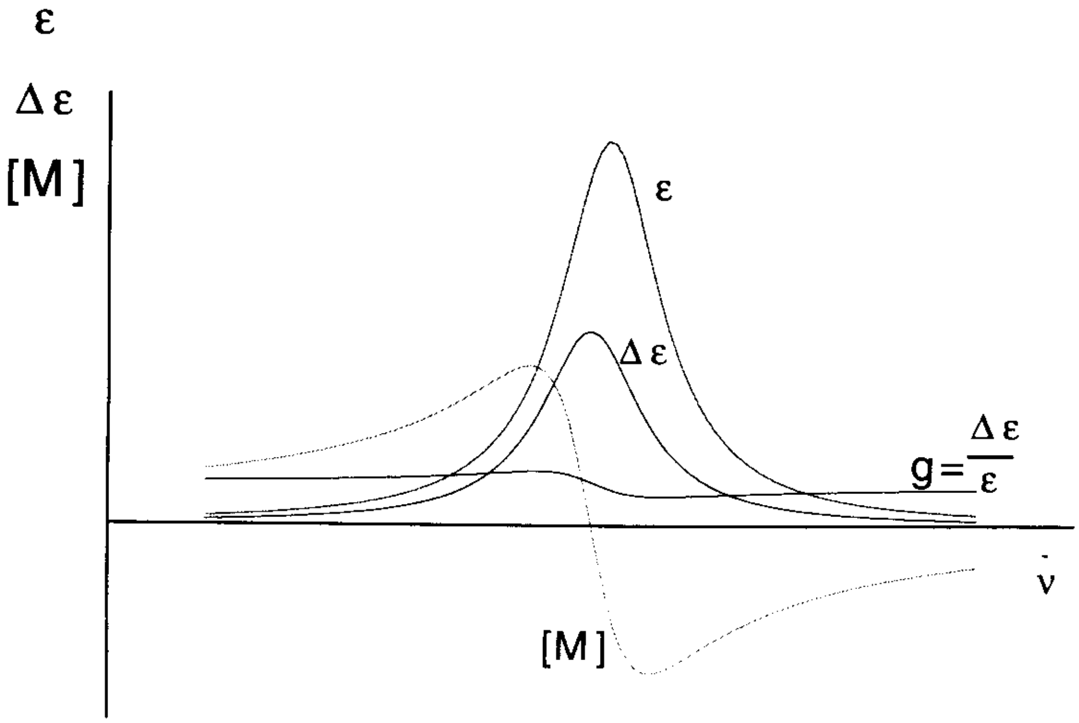


ellipticity $\mathrm{tg}\theta = \frac{b}{a} = 0.5757\{\varepsilon_L - \varepsilon_R\}cd \approx \theta;$

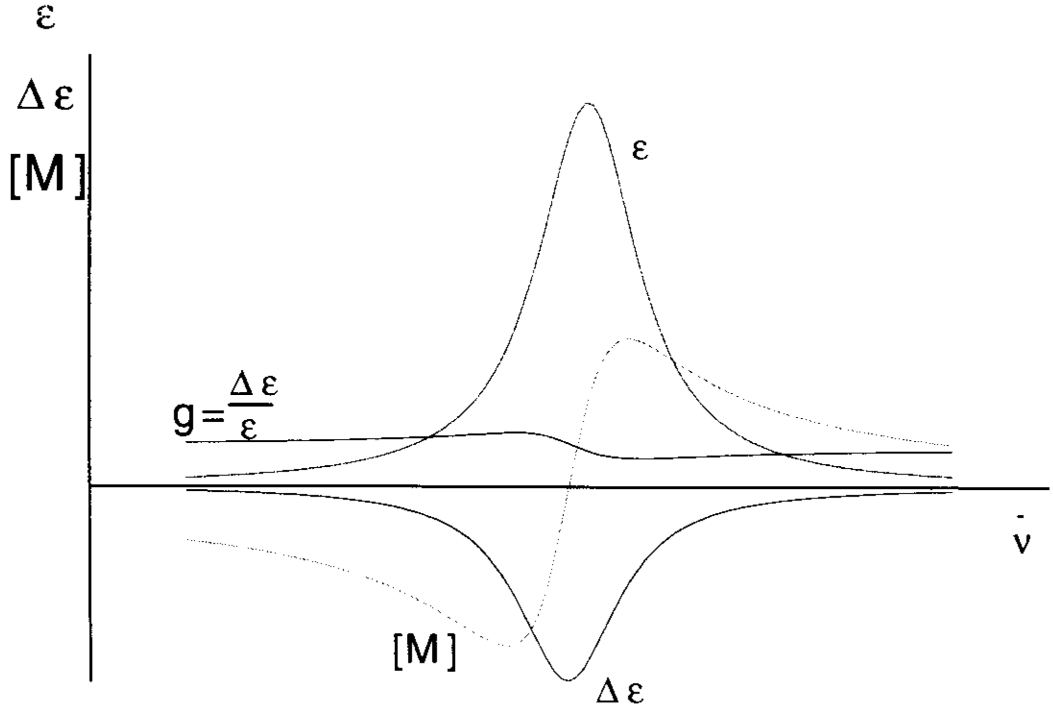
rotation $\Phi = \pi\bar{v}\{n_L - n_R\}$

$\Delta\varepsilon = \varepsilon_L - \varepsilon_R$

positive Cotton effect (CE)

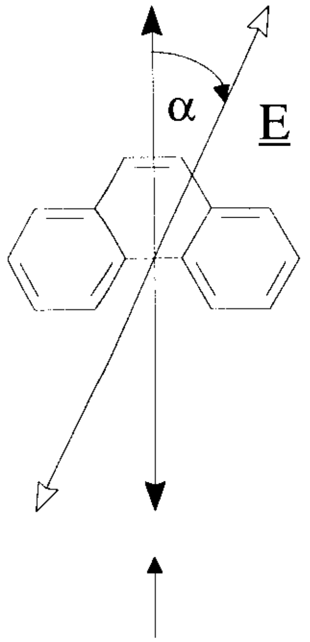


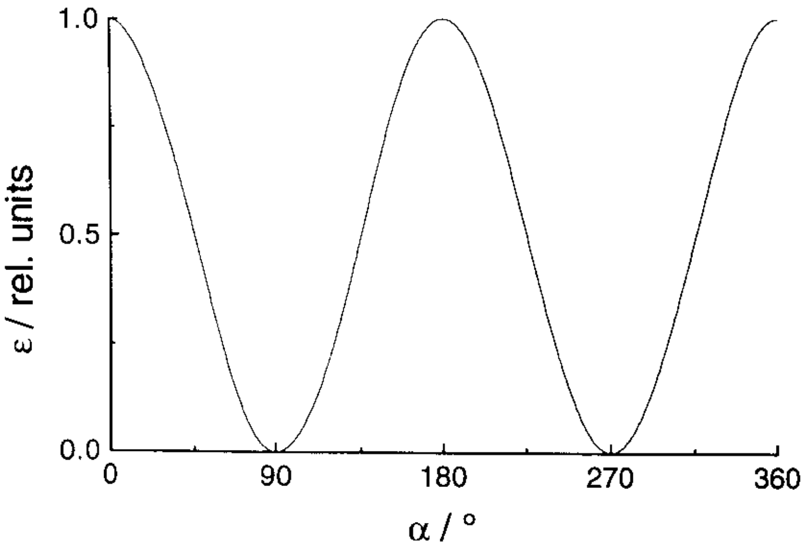
negative Cotton effect (CE)



Electric Dipole Transiton Moment Direction

Electric Dipole Transition Moment $\underline{\mu}_{ga}$





direction of polarization

$\varepsilon \sim \mu_{ga}^2$

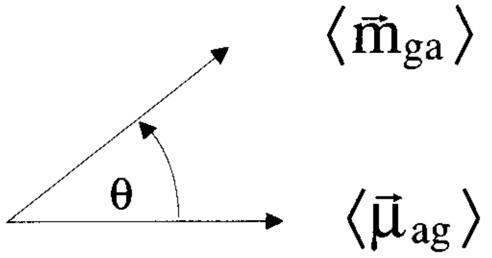
$\underline{\mu}_{ga} = \langle \psi_g | \hat{\underline{\mu}} | \psi_a \rangle$

$\hat{\underline{\mu}} = \sum_i q_i r_i$ dipole operator

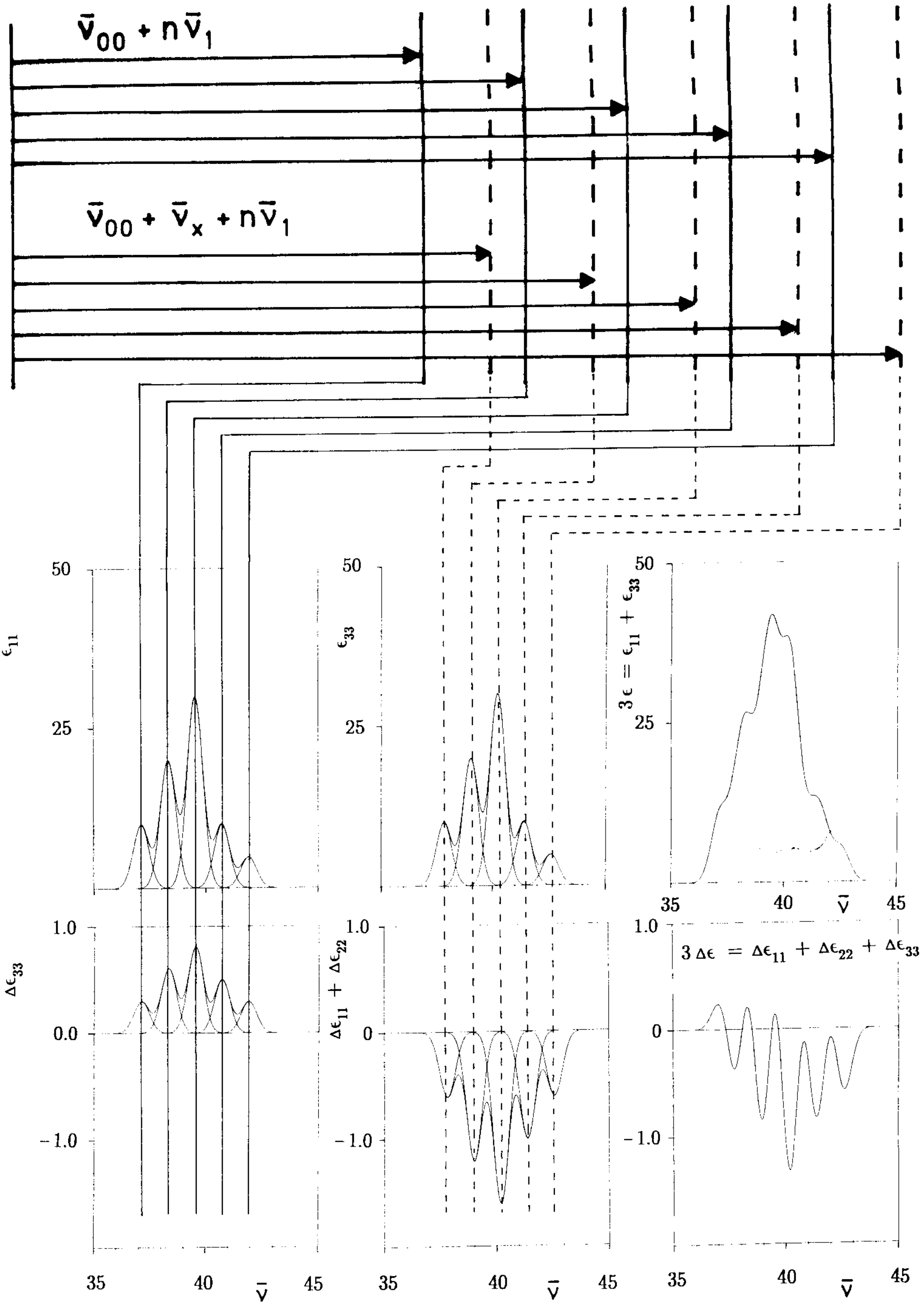
$\underline{E}$ electric field vector

Rotational Strength

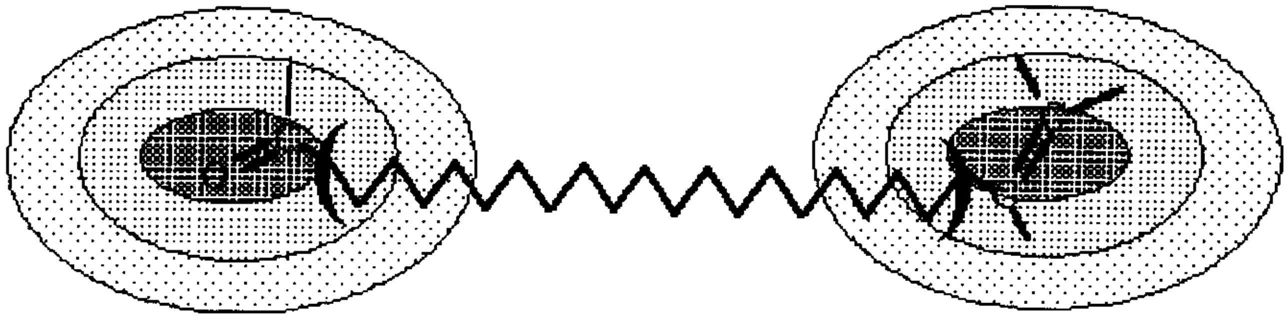
$$\Delta\varepsilon \approx R = \mathrm{Im}\left\{\langle \vec{\mu}_{ag} \rangle \cdot \langle \vec{m}_{ga} \rangle\right\}$$



$\langle \vec{\mu}_{ag} \rangle = \langle \varphi_g \lvert \hat{\mu} \rvert \varphi_a \rangle$	Electric Dipole Transitionmoment
$\langle \vec{m}_{ga} \rangle = \langle \varphi_a \lvert \hat{m} \rvert \varphi_g \rangle$	Magnetic Dipole Transitionmoment

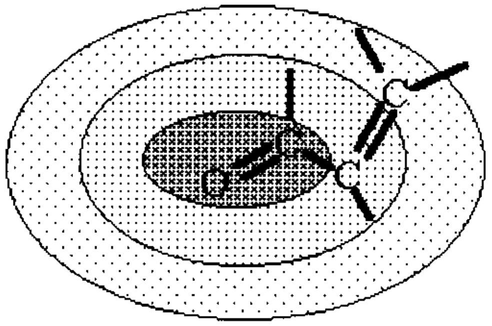

$\bar{\nu}_{00} + n\bar{\nu}_1$
$\bar{\nu}_{00} + \bar{\nu}_x + n\bar{\nu}_1$
ϵ_{11}
50
25
ϵ_{33}
50
25
$3\epsilon = \epsilon_{11} + \epsilon_{33}$
50
25
35
40
$\bar{\nu}$
45
$\Delta\epsilon_{33}$
1.0
0.0
−1.0
$\Delta\epsilon_{11} + \Delta\epsilon_{22}$
1.0
0
−1.0
$3\,\Delta\epsilon = \Delta\epsilon_{11} + \Delta\epsilon_{22} + \Delta\epsilon_{33}$
1.0
0
−1.0
35
40
$\bar{\nu}$
45
35
40
$\bar{\nu}$
45
35
40
$\bar{\nu}$
45

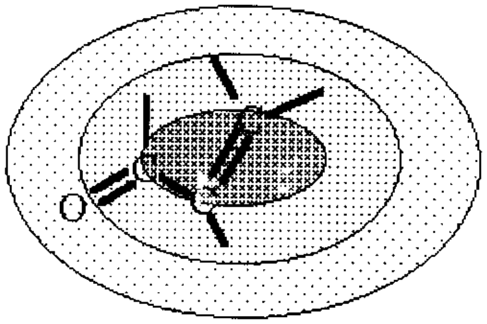
What does a „chromophore“ mean ?



$n\pi^*$: $\approx$ 290 nm

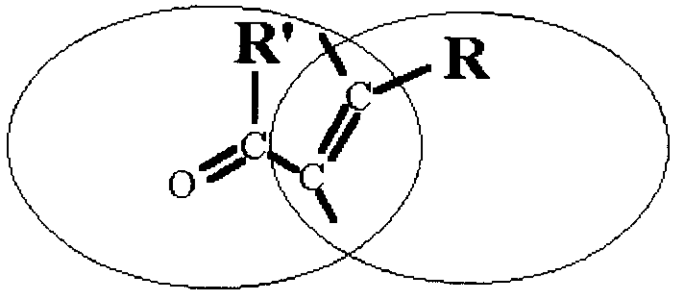
$\pi\pi^*$: $\approx \leq$ 200 nm



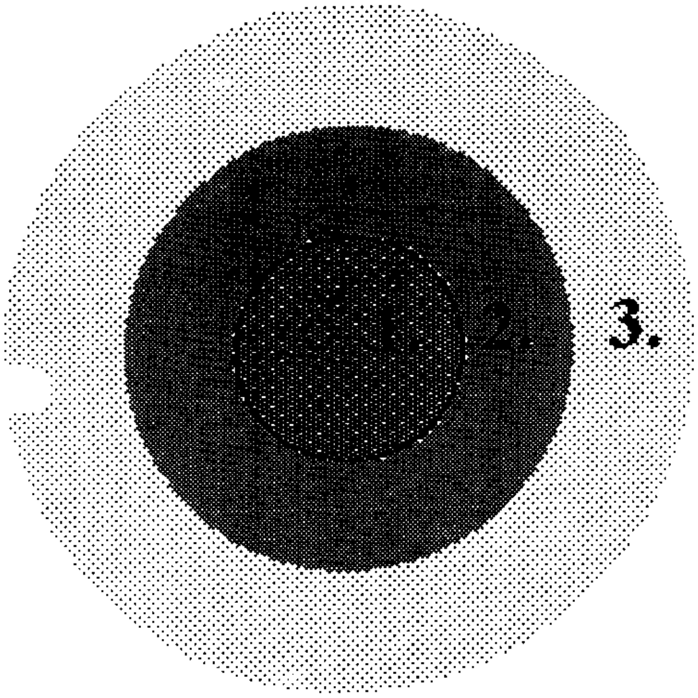


$n\pi^*/\pi\pi^*$: $\approx$ 340 nm

$\pi\pi^*/n\pi$: $\approx$ 230 nm



THE SPHERES



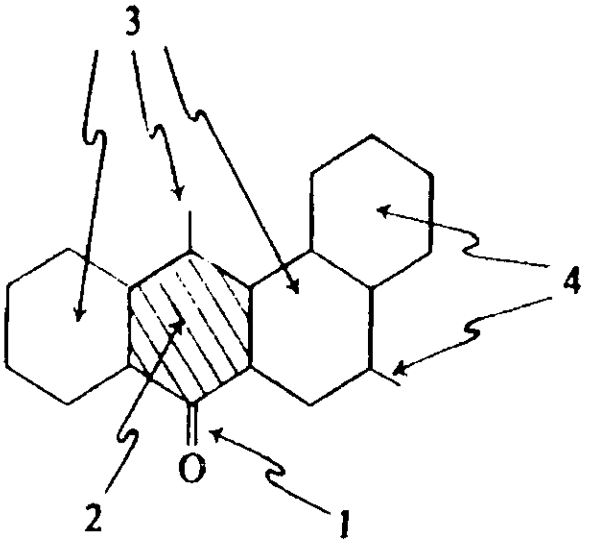
1. Sphere ≡ Chromophore

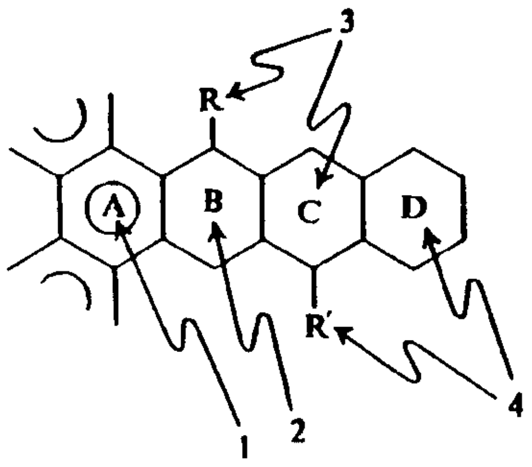
2. Sphere

3. Sphere

The distinction follows from the intensity of interaction

examples:





I

Methods / Rules for the Relation of the Sign of the Cotton Effects (CE) and the absolute Configuration

Chromophore (1. Sphere)

Surroundings (2., 3., ... Spere)

Sector Rules
(Ruch's Chirality Functions)

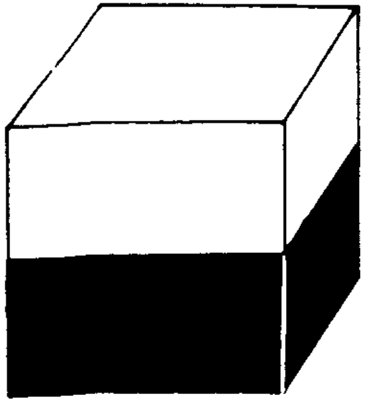
Helicity Rules

Exciton Chirality Method
(Coupling of Chromophores)

Qualitative Orbitalmodel

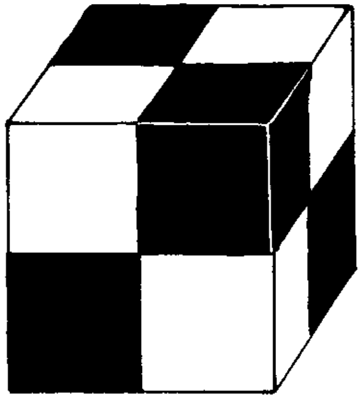
Quantum Mechanical Calculations
of the Rotational Strength
(Perturbation Theory)

SEKTORREGELN



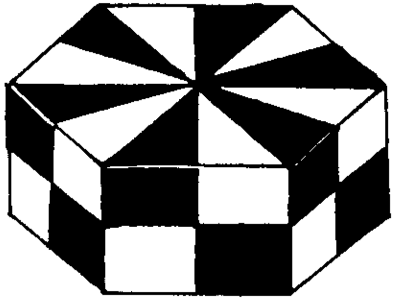
C_s C_{2h}

Z



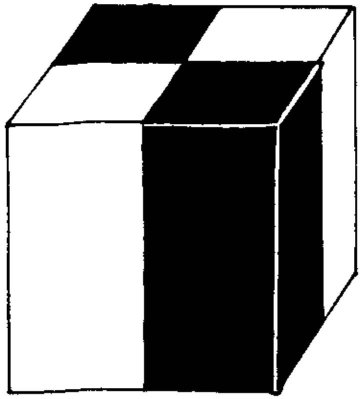
D_{2h}

XYZ



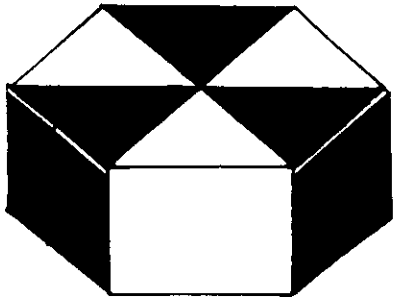
D_{6h}

$(Y^2 - 3X^3)(X^2 - 3Y^2)XYZ$



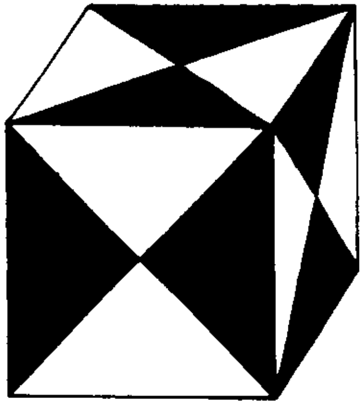
C_{2v}

XY



C_{3v}

$Y(3X^2 - Y^2)$



T_d

$(X^2 - Y^2)(Y^2 - Z^2)(Z^2 - X^2)$

Sector / Helicity Rules Derived for Different Chromophores

G. Snatzke und F. Snatzke,
Chirooptische Methoden in "Analytiker-Taschenbuch" Bd. 1
Eds.: H. Kienitz, R. Bock, W. Fresenius, W. Huber, G. Tölg
Springer-Verlag 1980

1. allenes

2. allyl alcohols

3. amines and their derivatives:
   α-substituted piperidines

4. N-salicylidene-derivatives of primary amines:
   a) NH_2 axial on the cyclohexane-ring
   b) derivatives of benzyl- and phenylethylamines

5. phthalimide-derivatives of primary amines

6. Cu-imidate-complexes of primary amines (in situ)

7. N-chlorine and N-bromine derivatives of secondary amines

8. dithiocarbamates of secondary amines

9. azides

10. azo compounds
    a) pyrazolines, with C=O substitution in α position
    b) trans-phenylazo compounds

11. azomethines

12. benzoates
    - a) monobenzoates
    - b) dibenzoates and benzene derivatives with similar transition moment

13. benzene chromophore
    - a) chiral mono-substituted benzene derivatives
    - b) tetralines, tetrahydroisoquinolines

14. biphenyls

15. carboxyl derivatives
    - a) saturated compounds
        - lactones
        - acids, esters, lactones
        - α-halogenated carboxylic acids and derivatives
        - α-amino- and α-hydroxy-acids
    - b) conjugated carboxyl derivatives
        - endocyclic
        - exocyclic (α-methylenebutyrolactones)
    - c) derivatives of homoconjugated carboxylic acids
    - d) satureted amines and lactams
        - ε-lactams
        - β-lactams
        - open-chain peptides

16. piperazine-diones

17. disulfides

18. dithiocarbonates (X=O)
    trithiocarbonates (X=S)

19. enolethers

20. thiiranes

21. flavanones

22. indole alkaloides

23. iodine alkanes

24. nitryloxy compounds

25. nitroalkanes
    a) axial nitrocyclohexane
    b) equatorial nitrocyclohexane
    c) 1-nitro-2-hydroxyalkanes

26. nitroxyl radicals

27. nucleosides, nucleotides
    a) pyrimidine glykosides
    b) purine glykosides

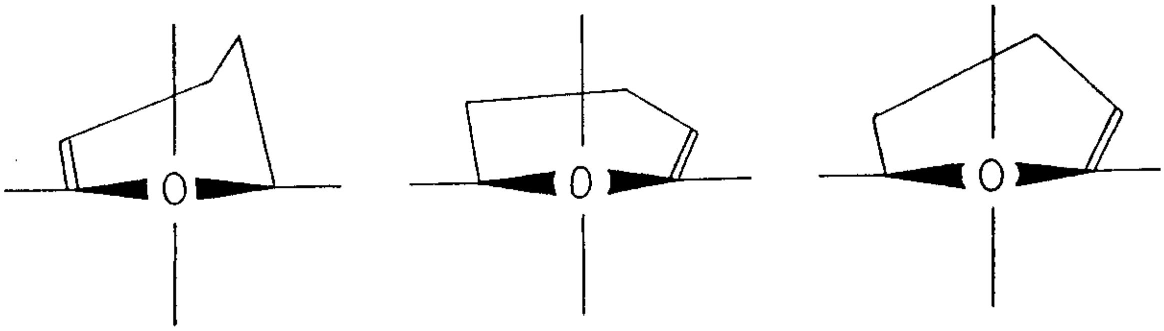
28. olefines
    a) isolated
    b) conjugated
    c) Pt-complexes of isolated olefins (in situ)

29. Oxathiolanes

30. oxo-compounds
    a) saturated
        without disturbing groups
            in the neighbourhood,
            aliphatic or in an achiral ring system

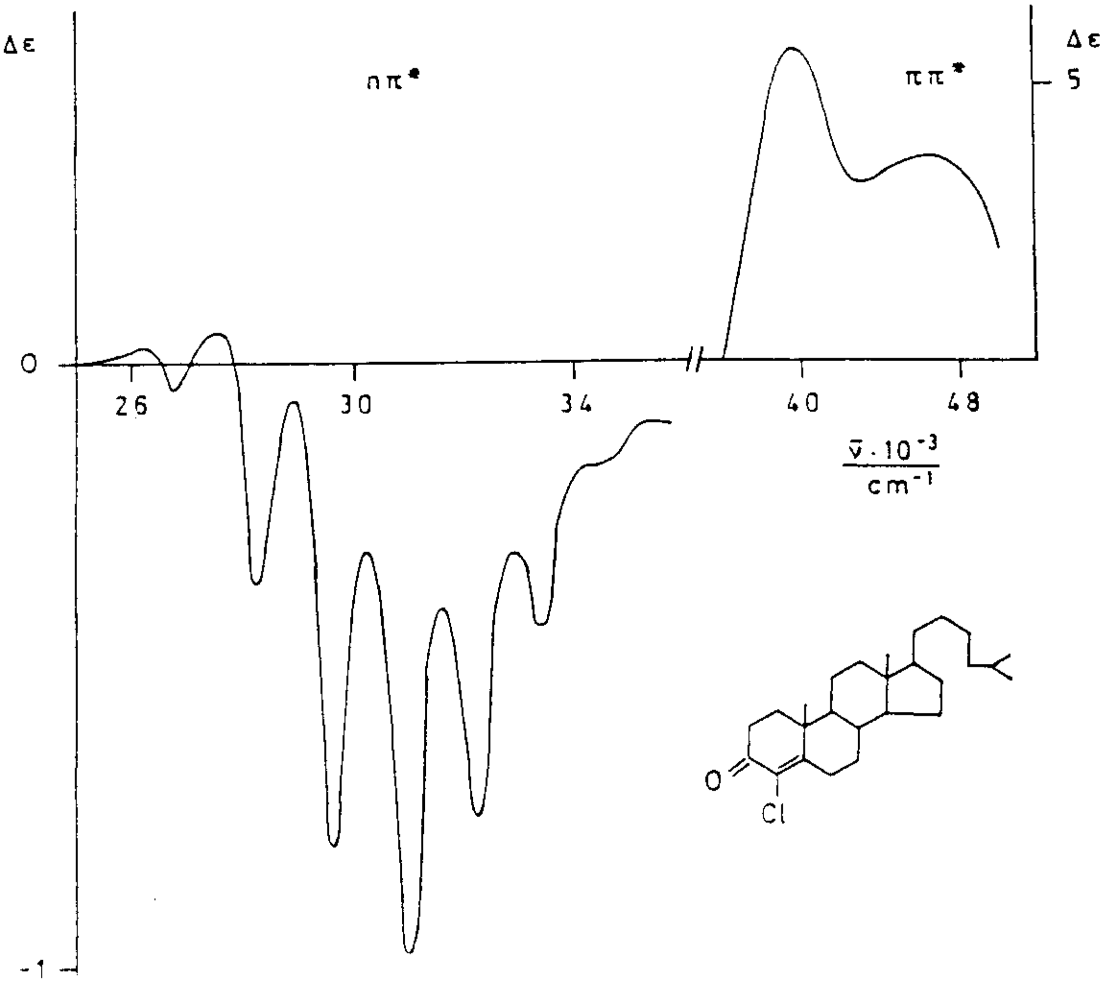
CONFORMATIONS OF THE A-RING

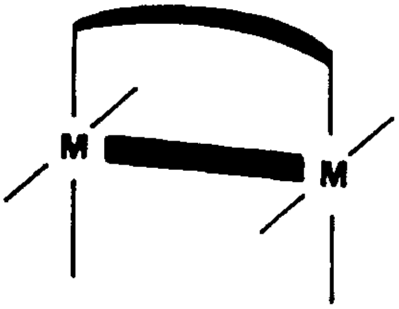
OF 4-EN-3-ONE-KETOSTEROIDS

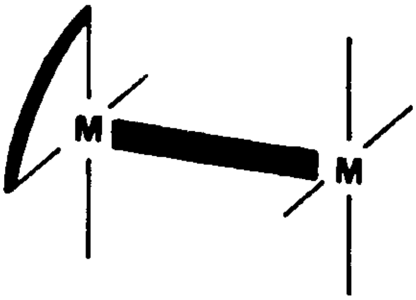


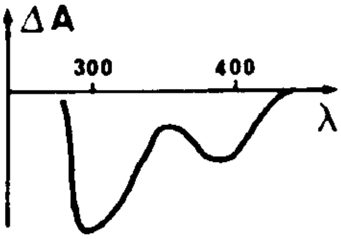
transition			
nπ*	– CE	+ CE	+ CE
ππ*	+ CE	– CE	– CE

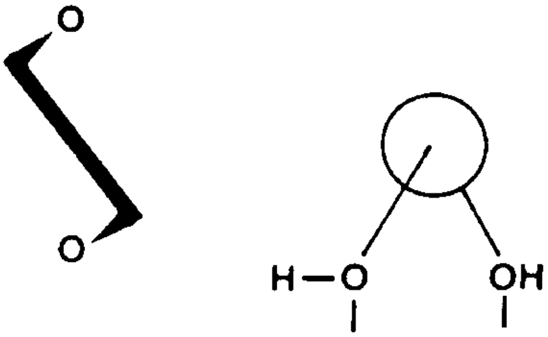
CE = Cotton effect

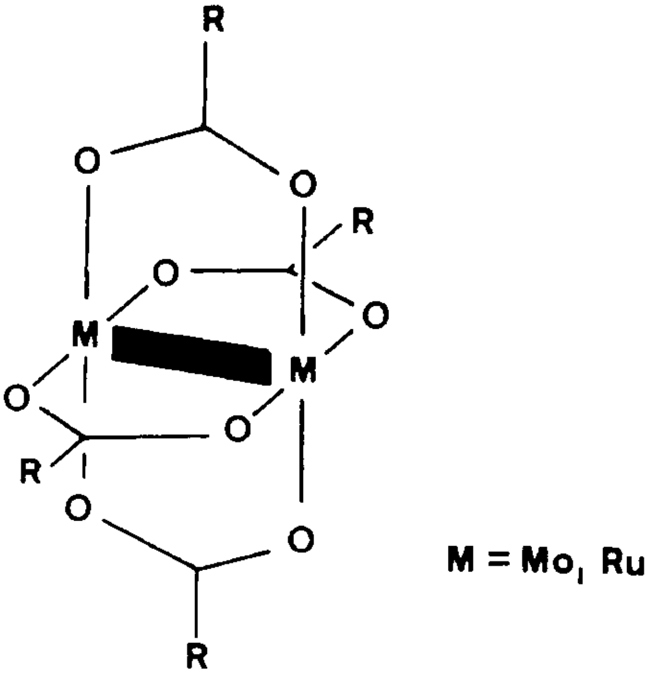






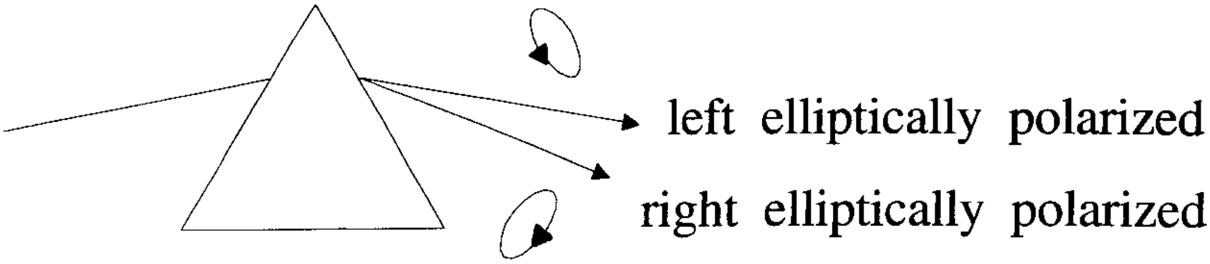


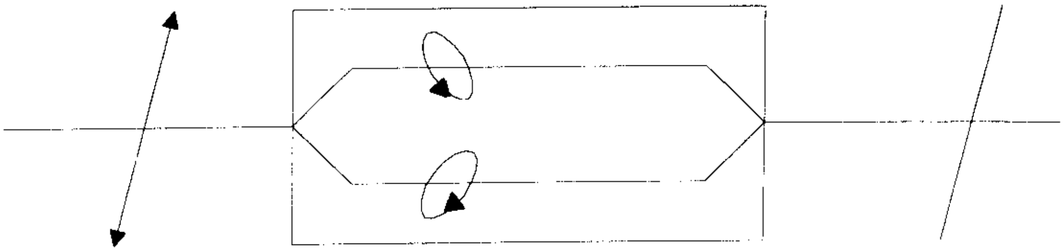




J. Frelek, Z. Majer, A. Perkowska, G. Snatzke, I. Vlahov und U. Wagner
Pure Appl. Chem. 57 (1985) 441

Elliptical Birefringence and Dichroism





split into two orthogonal elliptically polarized light beams with the

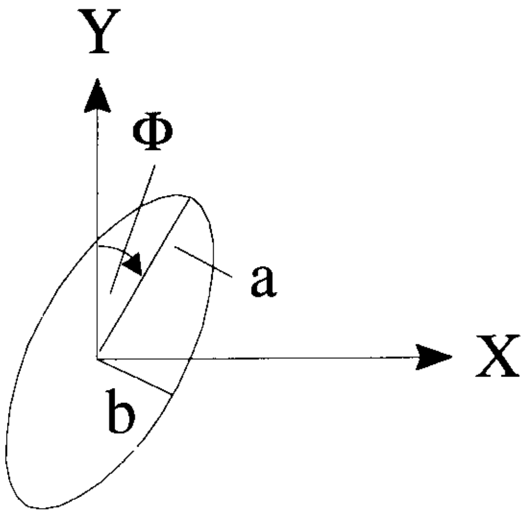
refraction indices n_{EL} or ε_{ER}
absorption coefficients ε_{EL} or ε_{LR}

for a sample without any symmetry propagating in an arbitrarily direction of the sample

special cases:

1. linear birefringence
   linear dichroism

2. circular birefringence
   circular dichroism



$\mathrm{tg}\,\theta = \frac{a}{b}$ ellipticity of light

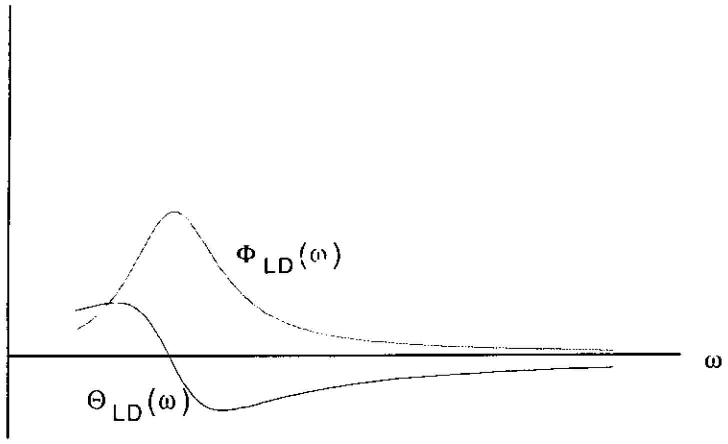
$\mathrm{tg}\,\Phi$ Φ optical rotation

assumption for small effects :

$$\hat{\Phi} = \Phi + i\Theta = \left(\Phi_{LD} + \Phi_{CD}\right) + i\left(\Theta_{LD} + \Theta_{CD}\right)$$

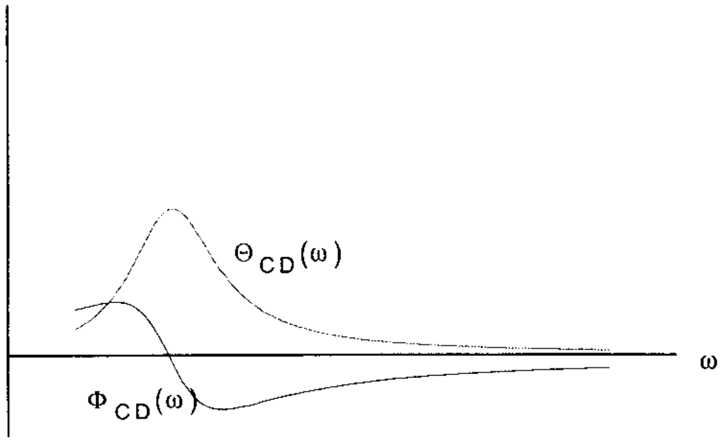
Linear Effect :

$$\Theta_{LD}(\omega) = -\frac{2}{\pi} \fint_{0}^{\infty} \frac{\omega' \Phi_{LD}(\omega')}{\omega'^2 - \omega^2} d\omega'$$



Circular Effect :

$$\Phi_{CD}(\omega) = +\frac{2}{\pi} \fint_{0}^{\infty} \frac{\omega \Theta_{CD}(\omega')}{\omega'^2 - \omega^2} d\omega'$$



$$\omega = 2\pi\nu = \frac{2\pi\bar{\nu}}{c}$$

Effects Conncted with Birefringence and Dichroism

second order optical phenomena in contrast
to first order optical phenomena: absorption of light
emission of light

Circular Effects

Faraday Effect	(MORD)
Magnetic Circular Dichroism	(MCD)
Optical Rotary Dispersion	(ORD)
Circular Dichroism	(CD)

Linear Effects

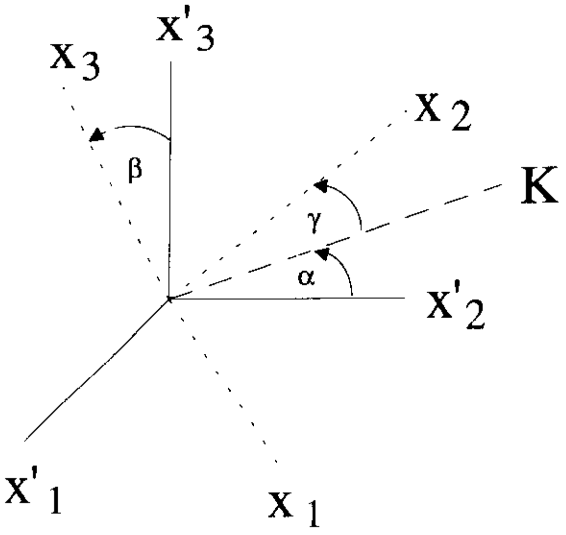
Kerr Effect
Electrochromism

Cotton Mouton Effect
Magnetic Dichroism

Linear Birefringence in Ordered Systems
Linear Dichroism in Ordered Systems
(polarized spectroscopy)

Ordered Systems : stretched polymers, liquid crystals, streaming fluids, etc.

ORIENTATION ORDER ONLY WITHOUT DYNAMICAL PROCESSES



α	$\alpha + d\alpha$
β	$\beta + d\beta$
γ	$\gamma + d\gamma$

probability : $f(\alpha, \beta, \gamma) \sin\beta \; d\alpha \; d\beta \; d\gamma$

example : solution in an electric field

$$f(\alpha, \beta, \gamma) = \frac{1}{Z} e^{-\frac{U(\alpha,\beta,\gamma)}{kT}}$$

$$U(\alpha, \beta, \gamma) = \underline{\mu}\underline{E} - \frac{1}{2}\underline{\tilde{E}}\underline{\underline{a}}\underline{E}$$

Z = partition function

Dipole Strength $D^{NK} = \left|\underline{\mu}_{ga}\right|^2$

Rotational Strength $R^{NK} = \operatorname{Im}\left\{\underline{\mu}_{ga} \cdot \underline{m}_{ag}\right\}$

$$\underline{\mu}_{ga} = \left\langle \psi_g \middle| \hat{\underline{\mu}} \middle| \psi_a \right\rangle$$

$$\underline{m}_{ag} = \left\langle \psi_a \middle| \hat{\underline{m}} \middle| \psi_g \right\rangle$$

$$\hat{\underline{\mu}} = \sum_i q_i \underline{r}_i$$

$$\hat{\underline{m}} = \sum_i \frac{Q_i}{2M_i} \underline{r}_i \times \hat{\underline{p}}_i$$

$$D^{NK} = 91.84 \cdot 10^{-40} \int \frac{\varepsilon(\overline{\nu})}{\overline{\nu}} d\overline{\nu} \qquad / \quad \text{cgs}$$

$$R^{NK} = 22.96 \cdot 10^{-40} \int \frac{\Delta\varepsilon(\overline{\nu})}{\overline{\nu}} d\overline{\nu} \qquad / \quad \text{cgs}$$

$$g = \frac{4R}{D} = \text{[illegible]} \frac{\left|\underline{m}_{ag}\right|}{\left|\underline{\mu}_{ga}\right|} \cos\angle\left(\underline{\mu}_{ga}, \underline{m}_{ag}\right)$$

$$\langle\vec{\mu}\rangle^{\alpha}_{\beta} = \frac{1}{\sqrt{2}}\left(\langle\vec{\mu}\rangle^{m}_{NK} \mp \langle\vec{\mu}\rangle^{n}_{NK}\right)$$

The − and the + sign correspond to the α and β transition, respectively.

$$\langle\vec{\mu}\rangle^{\alpha} = \sqrt{\frac{D^{NK}}{2}} \otimes$$

$$\{-2\sin\varphi\sin\gamma, 0, 2\cos\eta\cos\varphi\sin\gamma + 2\sin\eta\cos\gamma\},$$

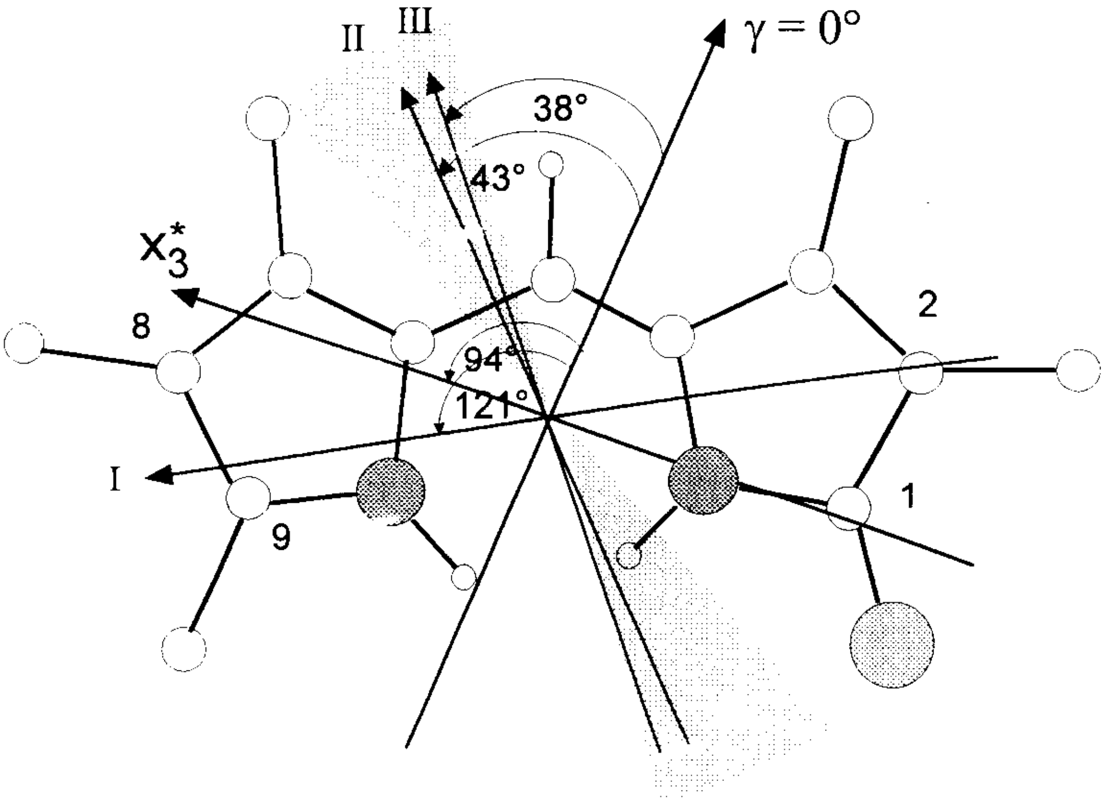
$$\langle\vec{\mu}\rangle^{\beta} = \sqrt{\frac{D^{NK}}{2}}\{0, -2\sin\eta\cos\varphi\sin\gamma + 2\cos\eta\cos\gamma, 0\},$$

$$D^{NK} = D^{NK,m} = \left|\langle\vec{\mu}\rangle^{m}_{NK}\right|^{2} = D^{NK,n} = \left|\langle\vec{\mu}\rangle^{n}_{NK}\right|^{2}$$

η is the angle between the C10 - C11 bond direction and the molecule-fixed x_2 axis (C_2 symmetry axis). γ is the angle between $\langle\vec{\mu}\rangle^{m}_{NK}$ and the C10 - C11 bond direction. φ the angle of rotation of the molecular plane of the dipyrrinone fragment m about the C10 - C11 bond direction (torsion angle). The angles η', γ' and φ' for the fragment n are defined analogously: $\eta' = 360° - \eta$ is the angle between the C10 - C9 bond direction $(\vec{t}')$ and the x_2 axis, $\gamma' = 360° - \gamma$ is the angle between the dipole transition moment $\langle\vec{\mu}\rangle^{n}_{NK}$ and the C10 - C9 bond direction.

$\varphi' = \varphi$. $\varphi = \varphi' = 0$ is the situation with the carbonyl group of the dipyrrinone fragments being oriented towards the x_2 axis.

$\vec{t}$ parallel to the C10 - C11 and the transition moment vector $\langle\vec{\mu}\rangle^{m}_{NK}$ and $\vec{t}$ span the plane of the dipyrrinone fragment m


II
III
$\gamma = 0°$
38°
43°
x_3^*
8
2
94°
121°
I
1
9