

# Chiroptical Properties of *cisoid* Enones from Circular Dichroism (CD) and Anisotropic Circular Dichroism (ACD) Spectroscopy

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**Abstract:** Substituted *cisoid* 4-en-6-one steroids with isotropically distributed and partially oriented molecules were analyzed by circular dichroism (CD) and anisotropic circular dichroism (ACD) spectroscopy, respectively. CD and ACD data supplement their respective phenomenological information. For a series of C3-substituted enones **1** to **7**, the difference of CD ( $\Delta\epsilon$ ) and ACD ( $\Delta\epsilon^A$ ) values, that is,  $\Delta\epsilon - \Delta\epsilon^A$ , vary in the  $n-\pi^*$  transition region in the same direction, independently of the nature and position ( $3\alpha$  or  $3\beta$ ) of the substituent. For  $7\alpha$ -bromo-substituted enones **5** and **6** the sign of the  $n-\pi^*$  CD band is opposite to that predicted by the enone helicity rule. The ACD data indicate that

this behavior is a consequence of the effect of vibronic coupling caused by the  $7\alpha$ -bromo substituent. In contrast to the results obtained for the series of C7-unsubstituted compounds **1** to **4**, the intensity of the CD bands for **5** and **6** is determined by the vibrational progressions of a different symmetry. Therefore, the helicity rule must fail in both cases because the rule can only be applied to those vibrational transitions for which the rule was developed. The sign of the

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coordinates  $\Delta\epsilon_{ii}^*$ , estimated from the ACD data, yields additional stereochemical information that cannot be obtained from the CD data alone. The CD and ACD spectra in the region of the  $\pi-\pi^*$  transition vary for enones **1** to **4** in a different fashion and indicate dependence upon spatial orientation ( $3\alpha$  or  $3\beta$ ) of substituents. This dependence may lead to the possibility of extracting additional stereochemical information from the ACD spectra. Furthermore, the experimental findings indicate that the second CD band located at about 220 nm belongs to a forbidden transition and not to an allowed  $\pi-\pi^*$  transition.

## Introduction

The  $\alpha,\beta$ -unsaturated ketones belong to the group of chromophores that have been investigated most extensively both experimentally and theoretically over the past decades. Circular dichroism (CD) spectra of enones usually show three or sometimes four CD bands in the range of 350 to 185 nm (28 500 to 54 000  $\text{cm}^{-1}$ ). The long wavelength band is an  $n-\pi^*$  transition which appears around 350 nm (28 500  $\text{cm}^{-1}$ ). The second band, which appears between 230–260 nm (38 500–43 500  $\text{cm}^{-1}$ ), is a  $\pi-\pi^*$  transition, polarized approximately

along the line connecting the oxygen and the most remote carbon atom of the C=C bond. According to the literature,<sup>[1, 2]</sup> the third CD band, which is found in the 200 to 220 nm spectral region (45 000 to 50 000  $\text{cm}^{-1}$ ) is likely a  $\pi-\pi^*$  transition. This assignment is not unequivocal because there is only a very small absorption intensity associated with this CD band. Thus, the dissymmetry factor  $\Delta\epsilon/\epsilon$  is too high for a  $\pi-\pi^*$  transition. Furthermore, the minimal frequency dependence of the linear dichroism in a stretched polyethylene film<sup>[2]</sup> or in an ordered liquid crystal phase<sup>[3]</sup> in this spectral region is not sufficient to give an unequivocal evidence for a second allowed  $\pi-\pi^*$  transition with a different polarization direction. The fourth band, which occurs around 185 nm (54 000  $\text{cm}^{-1}$ ), is assumed to result from the carbonyl  $n-\sigma^*$  transition.<sup>[4–7]</sup>

A series of various helicity and/or sector rules have been proposed to correlate the sign of the Cotton effects (CEs) that occur in the spectral region between 350 and 200 nm with the absolute configuration of *transoid* and *cisoid*  $\alpha,\beta$ -enone molecules.<sup>[5, 6]</sup> These rules are derived from the observation that the UV and CD spectra of enones are strongly influenced by substituents located in the vicinity of the chromophoric system. The presence of such substituents alters the enone

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chromophores with the respect to its spatial dimension as well as its electronic structure.<sup>[8–11]</sup> Therefore, helicity or sector rules have to be chosen with care. Recently we have reported a study on the chiroptical properties of *cisoid* enones, where, in general, the positive (negative) sign of the CE associated with the  $n-\pi^*$  transition reflects the positive (negative) enone helicity.<sup>[12]</sup> However, one of the examples discussed there indicated that substituents located in the vicinity of the chromophoric system may change the sign of the CD band without a corresponding change of the local helicity of the chromophore. There are additional literature reports indicating that the introduction of an  $\alpha'$ -axial bromo substituent leads to a sign change of the  $n-\pi^*$  CD band, for example, to a behavior contrary to the prediction based on the helicity rule.<sup>[4–6]</sup> Moreover, recently it has been reported that in the case of violascensol, belonging to the class of *cisoidal* enones, the general helicity rule is also not applicable. The CD spectrum of violascensol shows a negative CE in the range of the  $n-\pi^*$  band in contradiction to the positive enone helicity.<sup>[13]</sup>

The underlying reasons for an (apparent) break down of a helicity rule are varied. In the simplest case, a variation of the geometry of the chromophore caused by the presence of substituents may be responsible. Another possibility is based on an electronic interaction of the substituents placed in the vicinity of the chromophore. Thus, a spatial extension of the enone chromophore involving the O=C and/or C=C groups may arise that could lead to more or less stronger coupling or decoupling of these groups. Effectively, an inclusion of the substituent into the enone chromophoric system takes place. Consequently, a new rule has to be developed for this new chromophore to determine the sign of individual CEs, as in the case of Beecham's rule.<sup>[7]</sup> The failure of the enone helicity rules due to vibronic coupling has been suggested for the first time following the analysis of the anisotropic circular dichroism (ACD) data of oriented molecules obtained for a series of ketosteroids with various substituents in the vicinity of the enone chromophore.<sup>[10]</sup> The ACD measurements for ketosteroids with an additional ring system confirm this conclusion.<sup>[12]</sup> As a basis for this conclusion it has been demonstrated that the ACD data allow for the experimental determination of the contributions of different vibrational progressions to the CD band.<sup>[14–17]</sup>

The discussed above observations encouraged us to apply ACD spectroscopy systematically to solve stereochemical problems arising in attempts to correlate signs of CD bands and the absolute configuration of *cisoid* enone moieties. The aim of this paper is to report on the results of CD and ACD measurements of *cisoid* enones that have different substituents at the  $\alpha'$ - and/or  $\gamma$ -positions of the enone chromophore. In this paper we will discuss the basis of the ACD spectroscopy avoiding the mathematical analysis as much as possible.

## Experimental Section

To measure the circular dichroism spectrum of anisotropic samples (ACD)<sup>[11, 16, 17]</sup> nematic liquid crystal phases were used to align partially

dissolved chiral compounds (guest–host system). The chiral guest transforms the nematic phase into a cholesteric phase (chiral induction to a phase with suprastructural chirality<sup>[18]</sup>), which by itself exhibits a large CD and optical rotatory dispersion (ORD) bands as an inherent property of that phase. Therefore, for the ACD measurement the sample had to be transformed back into a chiral nematic phase without suprastructural chirality. For an induced cholesteric phase, in general, the suprastructural chirality<sup>[16–18]</sup> can be eliminated applying an electric AC or DC field large enough to unwind the helix ( $10^6 \text{ V m}^{-1}$ ). As a result, CD spectra can be measured<sup>[20]</sup> in the obtained uniaxial liquid crystal unidomain in a commercial CD instrument with the applied electric field parallel to the propagation direction of the light beam (optical axis of the phase).<sup>[16]</sup> The error of  $\Delta\epsilon$  is about 2% whereas that of  $\Delta\epsilon^A$  is around 5 to 20%.

By measuring the circular dichroism spectra with a linear polarized light beam propagating along the optical axis of the uniaxial liquid crystal (guest–host) phase, the ACD  $\Delta\epsilon^A$  is obtained; this can be related to the molecular quantities  $\Delta\epsilon_{ij}^*$  by Equation (1):

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

in which  $S^*$  and  $D^*$  are the Saupe order parameters given in respect to the molecule-fixed principal axes ( $x_i^*$ ) of the order tensor. The molecular quantities  $\Delta\epsilon_{ij}^*$  ( $i, j = 1, 2, 3$ ) are the coordinates of the circular dichroism tensor which are given here with respect to the  $x_i^*$  coordinate system:  $\Delta\epsilon_{11}^*$ .<sup>[11, 16]</sup> From a measurement of oriented molecules with the orientational distribution of a uniaxial sample with  $S^* = 1$  and  $D^* = 0$  (for which all molecules have their so-called orientation axis ( $x_3^*$ ) oriented parallel to each other, whereas the  $x_1^*$ ,  $x_2^*$  axes are distributed rotationally symmetric about this direction) and with a light beam propagating parallel to the  $x_3^*$  axis, Equation (2) can be derived from Equation (1):

$$\Delta\epsilon^A = \Delta\epsilon_{33}^* \quad (2)$$

Consequently,  $\Delta\epsilon_{33}^*$  is the result of a CD measurement with a light beam propagating along the  $x_3^*$  direction of the molecule and for which the molecules are distributed rotationally symmetric around this axis. For a measurement of  $\Delta\epsilon_{11}^*$  or  $\Delta\epsilon_{22}^*$  such a simple recipe cannot be given. However, these values can be rationalized in analogy to the measurement of  $\Delta\epsilon_{33}^*$  as a measurement with the light beams that propagate either along the  $x_1^*$  or the  $x_2^*$  direction. For these measurements molecules have to be distributed rotationally symmetric about the  $x_1^*$  and  $x_2^*$  axes, respectively. This means that by choosing three mutually perpendicular axis  $x_i^*$  ( $i = 1, 2, 3$ ) for such measurements, the CD data for the isotropic solution  $\Delta\epsilon$  can be given by the mean value of these results as shown in Equation (3):

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

For a uniaxial sample the second independent quantity  $\Delta\epsilon_2^A$  belongs to a CD measurement for a light beam propagating perpendicularly to the optical axis of the uniaxial sample. In the case of a real experiment such a measurement does not yield  $\Delta\epsilon_2^A$  directly because of the superposition of large contributions of linear birefringence and dichroism<sup>[16, 17]</sup> of the uniaxial phase. Therefore,  $\Delta\epsilon_2^A$  can be calculated by Equation (4):

$$\Delta\epsilon_2^A = \frac{1}{2}(3\Delta\epsilon - \Delta\epsilon^A) \quad (4)$$

In order to evaluate  $\Delta\epsilon_2^A$  by using Equation (4), the values of  $\Delta\epsilon$  have to be measured at the same temperature as  $\Delta\epsilon^A$ . While working with a liquid crystal matrix the  $\Delta\epsilon$  values can only be measured at temperatures above the clearing point. Thus, while applying Equation (4) one has to assume that the CD data is approximately temperature independent within the corresponding temperature range.

From measurements with samples different in order, for example, for different temperatures where the temperature dependence of  $S^*(T)$  and  $D^*(T)$  is known, the coordinates  $\Delta\epsilon_{33}^* - \Delta\epsilon = \frac{1}{3}(2\Delta\epsilon_{33}^* - \Delta\epsilon_{22}^* - \Delta\epsilon_{11}^*)$ , and  $\Delta\epsilon_{22}^* - \Delta\epsilon_{11}^*$  can be calculated by using Equation (1). Together with Equation (2), the quantities  $\Delta\epsilon_{11}^*$ ,  $\Delta\epsilon_{22}^*$ , and  $\Delta\epsilon_{33}^*$  can be then obtained.

If only the order parameter  $S^*$  can be estimated, the sign of  $\Delta\epsilon_{33}^*$  and  $\Delta\epsilon_{11}^*$  +  $\Delta\epsilon_{22}^*$  can be determined from the upper and lower limit given by Equations (5) and (6), respectively:

$$\Delta\epsilon^A \leq \Delta\epsilon_{33}^* S^* \leq \Delta\epsilon^A - \Delta\epsilon(1 - R_{\max}) \quad (5)$$

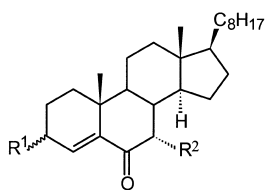
$$3\Delta\epsilon - \Delta\epsilon^A \leq (\Delta\epsilon_{11}^* + \Delta\epsilon_{22}^*) S^* \leq \Delta\epsilon(1 + 2R_{\max}) - \Delta\epsilon^A \quad (6)$$

$R_{\max}$  is the maximum of the degree of anisotropy  $R$  given by Equation (7), in which  $\epsilon_1$ ,  $\epsilon_2$ , and  $\epsilon = (\epsilon_1 + 2\epsilon_2)/3$  are the molar decadic absorption coefficients for light polarized parallel and perpendicular to the optical axis of a uniaxial sample and that of the isotropic solution, respectively:

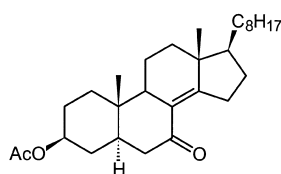
$$R(\bar{\nu}) = \frac{\epsilon_1 - \epsilon_2}{3\epsilon} \quad (7)$$

From the wavelength dependence, the intensity borrowing can be observed from the UV absorption band ( $\epsilon$ ) in connection with the polarized spectroscopy<sup>[21]</sup> by measuring the linear dichroism  $\epsilon_1 - \epsilon_2$ . Analogously to the values of  $\Delta\epsilon$  in the liquid crystal host phase, the values of  $\epsilon$  are not available experimentally for the same temperature as the polarized spectra  $\epsilon_1$  and  $\epsilon_2$  and thus for Equation (7) has to be used instead of the experimentally measured  $\epsilon$ .

The sources of compounds **1** to **7** are given in ref. [20]. ZLI-1695 (Merck mixture of four 4n-alkyl-4'-cyanobicyclohexanes) has been used as the liquid crystal host phase for orienting the *cisoid* enones throughout this paper.



- 1**  $R^1 = \alpha\text{-OAc}$ ;  $R^2 = \text{H}$     **4**  $R^1 = \beta\text{-Cl}$ ;  $R^2 = \text{H}$   
**2**  $R^1 = \beta\text{-OAc}$ ;  $R^2 = \text{H}$     **5**  $R^1 = \alpha\text{-OAc}$ ;  $R^2 = \text{Br}$   
**3**  $R^1 = \alpha\text{-Cl}$ ;  $R^2 = \text{H}$ ;    **6**  $R^1 = \beta\text{-OAc}$ ;  $R^2 = \text{Br}$



**7**

## Results and Discussion

**The  $n - \pi^*$  transition:** The intensity of the  $n - \pi^*$  absorption of compounds **1**, **2**, and **3** in ZLI-1695 is practically equal within 10 to 20 %. The UV spectra of enones **1–4** in the same solvent in its isotropic phase are similar to those recorded in acetonitrile. The absorption in acetonitrile is slightly enhanced (Table 1 and Figures 1–3). For the compound **4**, however, the absorption in both solvents is slightly enhanced in comparison to enones **1**, **2**, and **3**. The presence of  $3\beta$ -chloro substituent increases the values of the absorption coefficients in contrast to the  $3\alpha$ -chlorine as well as the  $3\alpha$ - and  $3\beta$ -acetoxy substituents. The  $7\alpha$ -bromo substitution leads to a strong increase of the intensity of the absorption coefficients for enones **5** and **6** in comparison to compounds **1** to **4**. Also in these cases the presence and orientation of the  $3\alpha$ - and  $3\beta$ -acetoxy substituents seem to have no influence on the size of the absorption. For enone **7** an absorption enhanced by a factor of about two in comparison to enones **1** to **3** has been found; this possibly originates from a different coupling between the  $\text{O}=\text{C}$  and the  $\text{C}=\text{C}$  group in rings B and C. Furthermore, the  $n - \pi^*$  band for compound **7** measured in ZLI is observed only as a shoulder at the foot of the  $\pi - \pi^*$  band (Table 1, Figure 4).

For the *cisoid* enones the degree of anisotropy  $R$  is smaller than the respective values for the *transoid* enones.<sup>[10]</sup> On one hand this is the effect of the inherent differences between the *cisoid* and *transoid* configuration and on the other hand an effect of the different spatial placement and orientation of the chromophore with the respect to the orientation axis. The 0–0 transition of the  $n - \pi^*$  transition is polarized with respect to the  $x_3^*$  axis about the magic angle because  $R \approx 0$  and  $S^* \neq 0$ , as can be concluded from  $R \approx 0.25$  of the  $\pi - \pi^*$  transition (Table 2). The degree of anisotropy  $R$  for the *cisoid* enones **1** to **4** increases with increasing wavenum-

Table 1. Absorption and circular dichroism data, and the degree of anisotropy  $R$  and the CD of anisotropic solutions (ACD;  $T = 38^\circ\text{C}$ ) of the *cisoid* enones **1** to **7** in Ace ( $T = 20^\circ\text{C}$ ) and isotropic ZLI-1695 ( $T = 80^\circ\text{C}$ ) for the  $n - \pi^*$  transition.

	Solvent	$\epsilon$ [ $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$ ] ( $\lambda_{\max}$ [nm])	$10^2 R$ ( $\lambda_{\max}$ [nm])	$\Delta\epsilon$ [ $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$ ] ( $\lambda_{\max}$ [nm])	$\Delta\epsilon^A$ [ $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$ ] ( $\lambda_{\max}$ [nm])
<b>1</b>	Ace	49.5 (321)		– 3.17 (328)	
	ZLI-1695	44.9 (324)	9.2 (324)	– 2.67 (333)	– 4.03 (337)
<b>2</b>	Ace	68.0 (320)		– 2.33 (326)	
	ZLI-1695	47.3 (324)	9.6 (324)	– 1.95 (331)	– 3.94 (333)
<b>3</b>	Ace	70.1 (323)		– 2.65 (330)	
	ZLI-1695	50.9 (321)	7.5 (319)	– 2.30 (335)	– 3.10 (338.5)
<b>4</b>	Ace	87.0 (330)		– 2.12 (328)	
	ZLI-1695	62.7 (326)	9.4 (326)	– 1.87 (333)	– 4.69 (336)
<b>5</b>	Ace	142.0 (339)		– 0.17 (370)	
				+ 0.79 (322)	
				– 0.06 (385)	
				+ 1.30 (330)	
<b>6</b>	Ace	147.4 (344)	– 4.1 (344)	– 0.06 (385)	– 2.60 (355)
				+ 1.33 (327)	
				– 0.03 (389)	
				+ 1.45 (330)	
<b>7</b>	Ace	95.9 (322)		– 1.06 (336)	
	ZLI-1695	95.5 (313 <sup>[a]</sup> )	27.1 (313)	– 1.39 (342)	– 2.59 (341)

[a] Shoulder.

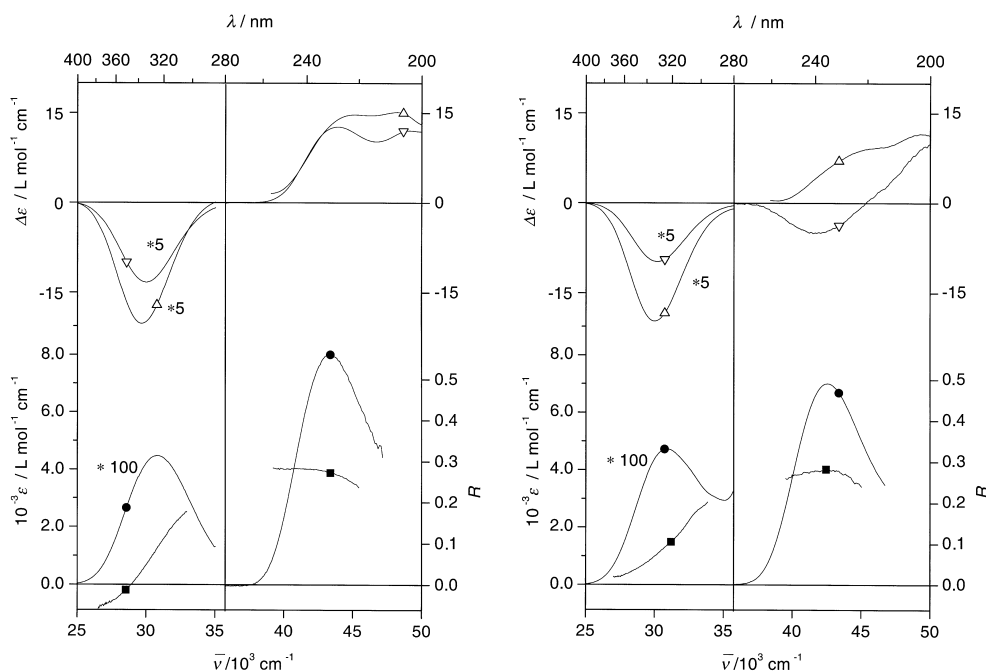


Figure 1. The  $\Delta\epsilon$  ( $\nabla$ ,  $T=80^\circ\text{C}$ ),  $\Delta\epsilon^A$  ( $\Delta$ ,  $T=38^\circ\text{C}$ ), UV spectra ( $\bullet$ ,  $T=80^\circ\text{C}$ ), and the degree of anisotropy  $R$  ( $\blacksquare$ ,  $T=38^\circ\text{C}$ ) of **1** (left) and **2** (right) in ZLI-1695 (Merck).

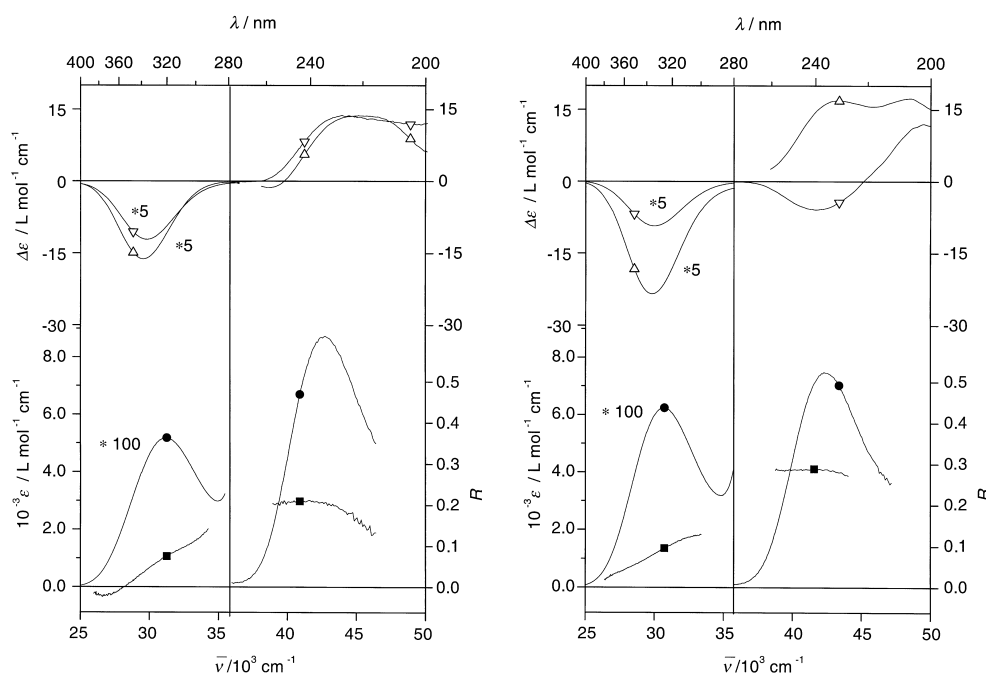


Figure 2. The  $\Delta\epsilon$  ( $\nabla$ ,  $T=80^\circ\text{C}$ ),  $\Delta\epsilon^A$  ( $\Delta$ ,  $T=38^\circ\text{C}$ ), UV spectra ( $\bullet$ ,  $T=80^\circ\text{C}$ ), and the degree of anisotropy  $R$  ( $\blacksquare$ ,  $T=38^\circ\text{C}$ ) of **3** (left) and **4** (right) in ZLI-1695 (Merck).

bers starting at the long wavelength side of the band from a negative value for **1** and **3** or a very small positive value for **2** and **4** (Figures 1 and 2). For 7 $\alpha$ -bromo-enones **5** and **6**, values of  $R$  decrease with increasing wavenumbers starting at the long wavelength side of the band from a small negative value for **5** and a small positive one for **6** and then increases to a value  $R \approx 0.05$  for **5** and  $R \approx 0.12$  for **6** (Figure 3). The observed wavenumber dependency of  $R(\tilde{\nu})$  indicates, unambiguously in case of enones **1** to **4** and with a high degree of

probability in the case of enones **5** and **6**, that there are at least two differently polarized absorption bands having their origin in different vibrational progressions. Furthermore, the different wavenumber dependence of  $R$  for enones **5** and **6** in comparison to compounds **1** to **4** points to the existence of strong influence of the bromine substituent on the enone chromophore leading to the enhancement of different vibrational progressions. From the change of the anisotropy of absorption  $R(\tilde{\nu})$  [Eq. (7)] for **5** and **6** in comparison with **1** to **4**

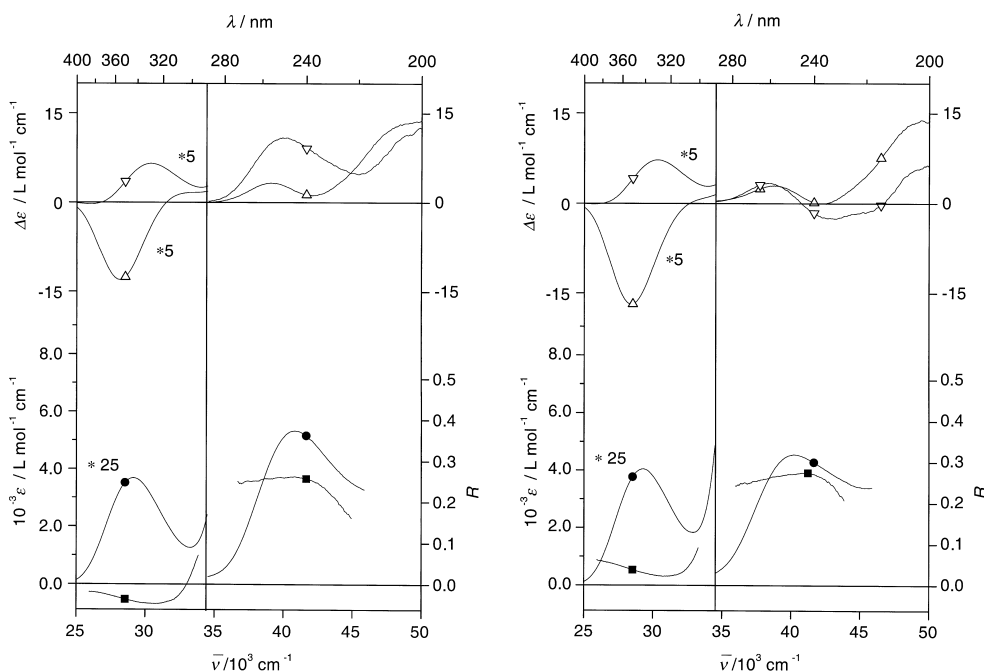


Figure 3. The  $\Delta\epsilon$  ( $\nabla$ ,  $T = 80^\circ\text{C}$ ),  $\Delta\epsilon^A$  ( $\Delta$ ,  $T = 38^\circ\text{C}$ ), UV spectra ( $\bullet$ ,  $T = 80^\circ\text{C}$ ), and the degree of anisotropy  $R$  ( $\blacksquare$ ,  $T = 38^\circ\text{C}$ ) of **5** (left) and **6** (right) in ZLI-1695 (Merck).

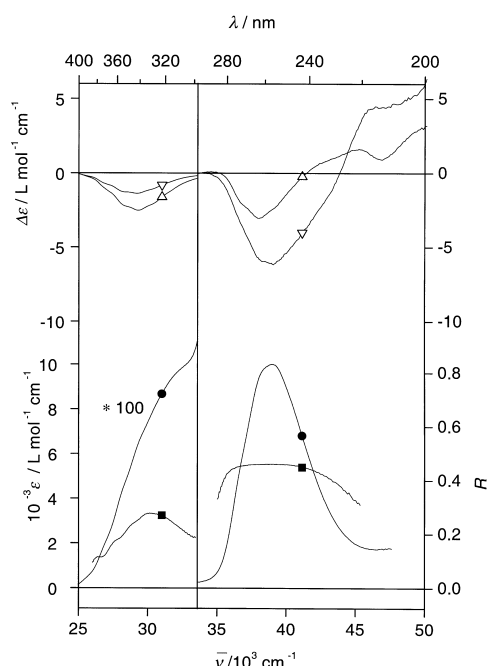


Figure 4. The  $\Delta\epsilon$  ( $\nabla$ ,  $T = 80^\circ\text{C}$ ),  $\Delta\epsilon^A$  ( $\Delta$ ,  $T = 38^\circ\text{C}$ ), UV spectrum ( $\bullet$ ,  $T = 80^\circ\text{C}$ ), and the degree of anisotropy  $R$  ( $\blacksquare$ ,  $T = 38^\circ\text{C}$ ) of **7** in ZLI-1695 (Merck).

to smaller positive values of  $R$  for **6** and negative values for **5**, it can be concluded that the progression with the transition moment direction perpendicular to the orientation axis (i.e., approximately the longest axis of the molecule) preferentially intensifies.

Whereas  $\Delta\epsilon$  is negative for **1** to **4** and **7**, a positive  $\Delta\epsilon$  is measured for **5** and **6** (Figures 1–4). For **5** and **6** a small negative “preband”<sup>[10]</sup> for the  $n-\pi^*$  transition is observed,

measured with larger concentration ( $c$ ) or pathlength ( $d$ ) (i.e., a larger product  $cd$ ) in acetonitrile as well as in ZLI-1695 (Table 1 and Figure 3). The ACD spectra of the *cisoid* enones **1** to **7** show an intensification of the  $n-\pi^*$  Cotton effect (CE) to larger negative values of  $\Delta\epsilon^A \approx -2.6$  to  $-4.7$ , whereas  $\Delta\epsilon^A$  for *transoid* 4-en-3-ones described before an increase from negative values of about  $-0.5$  to  $+0.9$  was observed.<sup>[10]</sup> Only as an exception are values found as high as  $+2.55$  to  $+2.20$ . Values of  $\Delta\epsilon^A$  are more negative than values of  $\Delta\epsilon$  for the *cisoid* enones **1**–**4** and **7** and changes from positive values of  $\Delta\epsilon$  to a negative  $\Delta\epsilon^A$  for **5** and **6** (Figures 1 to 4), that is,  $\Delta\epsilon^A - \Delta\epsilon < 0$  for all *cisoid* and  $\Delta\epsilon^A - \Delta\epsilon > 0$  for all *transoid* enones. Furthermore, the negative maxima of  $\Delta\epsilon^A$  of **1** to **7** when compared to the respective maxima of  $\Delta\epsilon$  are red-shifted.

The CD of the  $3\alpha$ -substituted compound **1** is larger than that of the  $3\beta$ -substituted compound **2**. The same although somewhat weaker effect can be seen for the chlorinated compounds **3** and **4**. In contrast, the ACD band is equal for **1** and **2**, whereas that of **4** is larger than that of **3**.

The qualitative discussion of the UV, linear dichroism (LD), CD, and ACD data confirm the conclusion that the sensitivity of the  $n-\pi^*$  transition of the enone chromophore due to the effects of substitution is in many cases related to the vibronic effects. The interpretation of the CD and LD can be based on the theoretical prediction that a different intensity of the CD band of different vibrational progressions leads to a different decrease or increase of the three quantities  $\Delta\epsilon_{ii}^*$  in  $\Delta\epsilon = \frac{1}{3}(\Delta\epsilon_{11}^* + \Delta\epsilon_{22}^* + \Delta\epsilon_{33}^*)$ . The variation of the coordinates  $\Delta\epsilon_{11}^*$ ,  $\Delta\epsilon_{22}^*$ , and  $\Delta\epsilon_{33}^*$  can be expressed quantitatively by a change of the electric and magnetic dipole transition moments, electric quadrupole transition moments, etc. In the one-electron or the dynamic-coupling model for CD, the interaction of the chromophore with its surroundings can be described by the mechanism of vibronic coupling. The

Table 2. Absorption and circular dichroism data, and the degree of anisotropy and the CD of anisotropic solutions (ACD;  $T = 38^\circ\text{C}$ ) of the *cisoid* enones **1** to **7** in Ace ( $T = 20^\circ\text{C}$ ) and of isotropic ZLI-1695 ( $T = 80^\circ\text{C}$ ) for the  $\pi-\pi^*$  transition.

	Solvent	$10^{-3}\epsilon$ [ $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$ ] ( $\lambda_{\text{max}}$ [nm])	$10^1 R$ ( $\lambda_{\text{max}}$ [nm])	$\Delta\epsilon$ [ $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$ ] ( $\lambda_{\text{max}}$ [nm])	$\Delta\epsilon^A$ [ $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$ ] ( $\lambda_{\text{max}}$ [nm])
<b>1</b>	Ace	8.71 (230)		+ 14.2 (226) + 14.8 (201)	
	ZLI-1695	8.01 (231)	2.72 (231)	+ 11.8 (229) + 11.4 (200) <sup>[a]</sup>	+ 13.4 (222) + 14.4 (207)
<b>2</b>	Ace	7.20 (233)		− 4.8 (237) + 13.2 (197)	
	ZLI-1695	7.01 (235)	2.79 (235)	− 5.0 (241) + 10.0 (200) <sup>[a]</sup>	+ 9.3 (217) + 11.6 (203)
<b>3</b>	Ace	7.81 (234)		+ 15.6 (225) + 15.1 (212)	
	ZLI-1695	8.74 (235)	2.07 (234)	+ 13.8 (226) + 12.9 (212)	+ 13.7 (226) + 12.9 (212)
<b>4</b>	Ace	9.30 (238)		− 6.0 (237) + 14.4 (200)	
	ZLI-1695	7.46 (236)	2.86 (236)	− 5.5 (241) + 11.2 (200) <sup>[a]</sup>	+ 14.7 (230) + 15.7 (205)
<b>5</b> <sup>[b]</sup>	Ace	6.00 (246)		+ 10.3 (251) + 6.5 <sup>[c]</sup> (229) + 8.7 (202)	
	ZLI-1695	5.34 (245)	2.62 (245)	+ 10.9 (251) + 12.5 (201)	+ 3.3 (257) + 13.6 (201)
<b>6</b> <sup>[b]</sup>	Ace	5.00 (249)		+ 4.4 (260) − 2.3 (233) + 2.8 (202)	
	ZLI-1695	4.56 (249)	2.72 (249)	+ 3.4 (261) − 2.6 (231) + 6.4 (201)	+ 3.0 (258) + 13.9 (203)
<b>7</b>	Ace	9.55 (258)		− 4.9 (259) + 5.0 (215)	
	ZLI-1695	9.85 (257)	4.60 (257)	− 5.4 (259) + 4.5 (200) <sup>[a]</sup>	− 2.2 (263) + 1.9 (221)

[a] Maximum not reached before 200 nm. [b] Slow decomposition in solution. [c] Shoulder.

forbidden electric dipole  $n-\pi^*$  transition borrows intensity from allowed electric dipole transitions of the same chromophore (one-electron model) or from chromophores of the surroundings (dynamic-coupling model).<sup>[8–11]</sup> By this mechanism normal vibrations of different symmetry of the chromophore change the intensity of absorption differently. This means that different vibrational progressions contribute with different intensity to the UV absorption and also with different intensity to the CD spectrum of the transition  $|N\rangle \rightarrow |K\rangle$  ( $K=1, 2, 3, \dots$ ). Whereas for the UV data only positive contributions exist, the CD of different progressions contribute with a positive or negative values to the CD band.<sup>[9, 14, 15]</sup> Therefore, a sign change of  $\Delta\epsilon$  may occur without a corresponding change of the local absolute configuration by intensifying positive or negative contributions caused by the substituents. For this the coordinates  $\Delta\epsilon_{ii}^*$  have to be enhanced or diminished to such an extent that the sum over the coordinates  $\Delta\epsilon_{jj}^*$  with  $j \neq i$  is different in sign from that of the reference compound. This means also that the main intensity of the CD band of the series of compounds differing only in substitution pattern may be determined by vibrational progressions other than the band of the unsubstituted reference compound. In such a case direct application of the helicity or sector rules is not allowed because the CD data measured for both investigated and reference compounds would belong to the different vibrational transitions of the

chromophore. In other words, the rules can only be applied to the CD of molecules if the CD bands can be traced back to the same type of transitions, for example, to the same progression of vibration. Otherwise the rules can fail.

**The  $\pi-\pi^*$  transition:** In accordance with the literature,<sup>[2]</sup> compounds **1** to **7** possess only one band in the UV region between 200 and 260 nm (Figures 1–4). Their CD spectra exhibit two bands for **1** to **4** and **7**, two bands and one shoulder for **5**, and three bands and one shoulder for **6** (Figures 1–4). The distance between both well developed CD maxima in **1** to **7** varies from 4000 to 7000  $\text{cm}^{-1}$ . The maximum of the UV absorption corresponds to the long wavelength CD maximum arising around 220 to 260 nm. Although there is neither a second band nor a shoulder in the absorption curve between 200 and 260 nm, there is a frequency dependence of the degree of anisotropy  $R$  in the flank of the UV band in the long wavelength and in the short wavelength area (Figures 1–4). The decrease of  $R$  values found in the range between 220 and 200 nm may be a consequence of the presence of a second band with a different polarization direction hidden under the main band.<sup>[2]</sup> However, one has to be very careful with such argumentation. The frequency dependence of  $R$  values upon the long and short wavelength flank of the UV band may also be the consequence of a solvent-dependent shift of the anisotropic absorption  $\epsilon_1(\lambda)$  with respect to the anisotropic

absorption  $\varepsilon_2(\lambda)$  [Eq. (7)] or alternatively to a small and independent change of the bandwidth of both bands.

Because of the partial overlapping of the  $n-\pi^*$  and  $\pi-\pi^*$  regions, the error of  $\Delta\varepsilon^A$  is higher than that of  $\Delta\varepsilon$  for **1** to **7**, and thus the quantitative discussion should be limited to general conclusions only. For the differently substituted 4-en-6-ones **1** to **6**, the second CD and ACD band around 200 to 220 nm (band II) has the same sign and approximately the same size. However, the  $\pi-\pi^*$  CD and ACD band I occurring around 220 to 260 nm is highly anisotropic. Furthermore, it is interesting to note that in the  $\pi-\pi^*$  band I region of the enones **1** to **4** the ACD band is always positive, whereas the CD band is positive ( $\Delta\varepsilon > 0$ ) for the  $3\alpha$ -substituted compounds **1** and **3** and negative ( $\Delta\varepsilon < 0$ ) for the  $3\beta$ -substituted compounds **2** and **4** regardless of the type of substituent. This means that the presence of  $3\alpha$ - and  $3\beta$ -substitution changes one or two of the coordinates  $\Delta\varepsilon_{ii}^*$  in a different manner (see also next section). As a result, the ACD effect  $\Delta\varepsilon^A - \Delta\varepsilon$  is about zero for the  $3\alpha$ -substituted compounds and large and positive for the  $3\beta$ -substituted compounds in the region 220 nm to 260 nm. These findings indicate that comparison of  $\Delta\varepsilon^A$  and  $\Delta\varepsilon$  may yield additional information about the stereochemistry of the substituent present at the  $\gamma$ -allylic position. The 7-bromine substitution in **5** and **6** has a strong influence on the absorption of the enone chromophore in the region below 280 nm. In case of enone **6** a new apparent negative CD band can be seen. The ACD bands of both compounds **5** and **6** are positive but their intensity is strongly reduced in comparison to the CD bands of parent acetoxy-enones **1** and **2**, respectively.

The origin of the sign change of  $\Delta\varepsilon$  and the bi-sigmoidal CD curves in the 200 nm to 260 nm spectral range, apparently caused by the bromine substituent, cannot be understood well at the moment. The axial substitution at  $\alpha'$  and  $\gamma$ -transoid allylic positions causes a strong electronic change of the enone chromophore. Thus, a different intensification of the three coordinates  $\Delta\varepsilon_{ii}^*$  can follow as a consequence of the change of the electronic transition; this can also lead to a sign change of  $\Delta\varepsilon$  without a corresponding change of the local absolute configuration in the enone area. Such a perturbation of the chromophoric system can serve as partial explanation for the generalized Beecham's rule<sup>[19]</sup> for  $\gamma$ -substituted enones. Moreover, in addition to that electronic effect, a pure enlargement of the enone chromophoric area by the axial substitution at  $\alpha'$  and  $\gamma$ -transoid allylic positions also takes place, and thus different helicities can be "seen" by the electronic excitation. Here, either the O=C or

C=C groups can be more involved. As a result, a stronger coupling or decoupling of involved groups yields in a different change of the three coordinates  $\Delta\varepsilon_{ii}^*$ .

For enone **7**, unsubstituted in the vicinity of the chromophore,  $\Delta\varepsilon^A$  keeps the sign of  $\Delta\varepsilon$  both for band I present at 263 nm and for band II occurring at 221 nm. The intensity of both ACD bands is reduced relative to the corresponding CD bands, that is,  $|\Delta\varepsilon^A(\mathbf{7})| < |\Delta\varepsilon(\mathbf{7})|$ .

**Estimation of the sign of the  $\Delta\varepsilon_{ii}^*$  for the  $n-\pi^*$  and  $\pi-\pi^*$  transition:** Additional stereochemical properties can be expected from the sign and size of the tensor coordinates  $\Delta\varepsilon_{ii}^*$ , because these quantities represent an outcome of views along different directions  $i = 1, 2$ , and  $3$  of the frame of the molecules as discussed above. Furthermore, the tensor coordinates  $\Delta\varepsilon_{ii}^*$  provide, in addition to the linear dichroism, new information about the normal vibrations contributing to UV and CD spectra. The latter are important to analyze the effect of intensity borrowing of electric dipole forbidden transition with respect to the sign of the CE and, thus, allow to examine the validity of helicity rules and to test their limits of applicability.

In order to avoid costly and time-consuming syntheses of different  $[D_1]$  to  $[D_5]$ -deuterated compounds<sup>[15]</sup> and the  $^2\text{H}$  NMR measurements to determine order parameters to evaluate the  $\Delta\varepsilon_{ii}^*$ , an attempt will be made to estimate their sign from the CD, ACD, and the linear dichroism measurements.<sup>[10, 22]</sup> Neglecting the biaxiality term  $(\Delta\varepsilon_{22}^* - \Delta\varepsilon_{11}^*)D^*/\sqrt{3}$  in Equation (1),<sup>[10]</sup> the limiting curves as shown as an example for compounds **1**, **2**, and **5** (Figures 5 and 6) can be evaluated according to the Equations (5) and (6). The correct curves for  $\Delta\varepsilon_{33}^*S^*$  and  $(\Delta\varepsilon_{11}^* + \Delta\varepsilon_{22}^*)S^*$  must be found in the area between these limiting curves. From these curves the sign of  $\Delta\varepsilon_{33}^*$  and

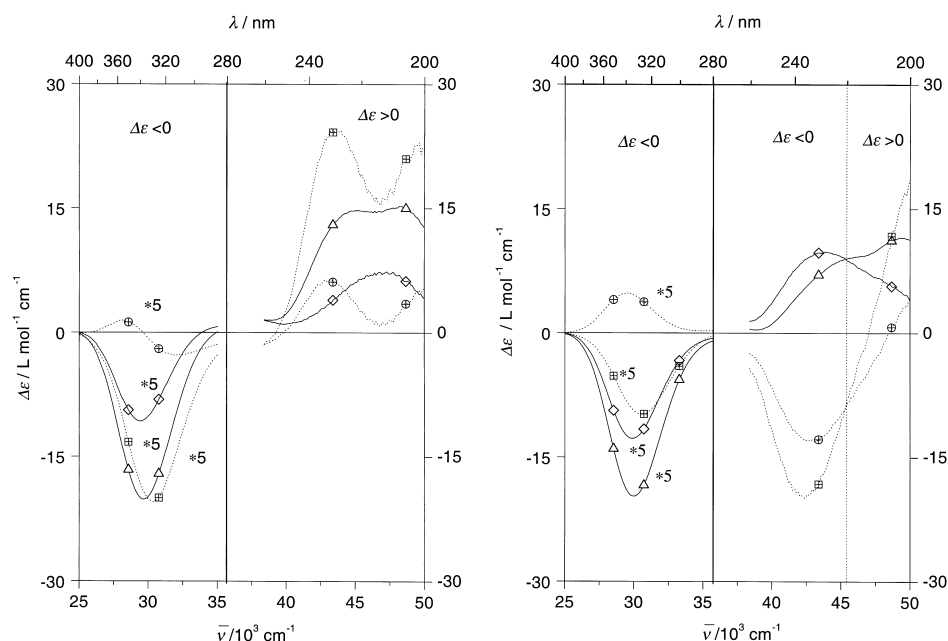


Figure 5.  $\Delta\varepsilon^A$  ( $\Delta$ ) and  $\Delta\varepsilon^A - \Delta\varepsilon(1 - R_{\max})$  ( $\diamond$ ) as an upper and lower limiting curves for the estimation of the sign of  $\Delta\varepsilon_{33}^*$  according to Equation (5) and  $3\Delta\varepsilon - \Delta\varepsilon^A$  ( $\blacksquare$ ) and  $\Delta\varepsilon(1 + 2R_{\max}) - \Delta\varepsilon^A$  ( $\blacksquare$ ) for the estimation of the sign of  $\Delta\varepsilon_{11}^* + \Delta\varepsilon_{22}^*$  according to Equation (6) for **1** (left) and **2** (right) in ZLI-1695. For **3** and **4** similar results were obtained.<sup>[23]</sup>

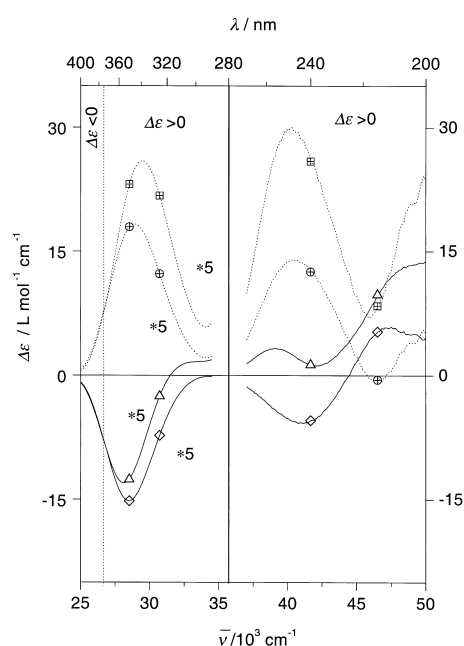


Figure 6.  $\Delta\epsilon^A$  ( $\Delta$ ) and  $\Delta\epsilon^A - \Delta\epsilon(1 - R_{\max})$  ( $\diamond$ ) as an upper and lower limiting curves for the estimation of the sign of  $\Delta\epsilon_{33}^*$  according to Equation (5) and  $3\Delta\epsilon - \Delta\epsilon^A$  ( $\blacksquare$ ) and  $\Delta\epsilon(1 + 2R_{\max}) - \Delta\epsilon^A$  ( $\bullet$ ) for the estimation of the sign of  $\Delta\epsilon_{11}^* + \Delta\epsilon_{22}^*$  according to Equation (6) for **5** in ZLI-1695. For **6** a similar results is obtained except that the sign of the curves in the  $\pi\pi^*$  region is reversed.<sup>[23]</sup>

$(\Delta\epsilon_{11}^* + \Delta\epsilon_{22}^*)$  can be derived (Table 3) because  $S^* \geq 0$ . From Figures 5 and 6 it follows that  $\Delta\epsilon_{33}^*$  is negative in the spectral region of the  $n-\pi^*$  absorption for the *cisoid* enones **1** to **6**. If both curves limit the areas of different sign as shown in Figure 5 for  $(\Delta\epsilon_{11}^* + \Delta\epsilon_{22}^*)S^*$ , for the assessment of the sign of  $\Delta\epsilon_{33}^*$  the value of  $S^*$  has to be estimated. Assuming that the maximum of the degree of anisotropy  $R = R_{\max}$  (Figures 1–3) in the  $\pi-\pi^*$  transition is approximately equal to the order parameter  $S^* < 0$  it follows that for **1** and **3** the values of  $(\Delta\epsilon_{11}^* + \Delta\epsilon_{22}^*)$  in the  $n-\pi^*$  region are small, and the wavelength dependence may have a sigmoidal structure. For the enone **2** the value of  $(\Delta\epsilon_{11}^* + \Delta\epsilon_{22}^*)$  is small and positive in this region, whereas this sum is large and positive for **4** to **6**.

Because  $|\Delta\epsilon_{11}^* + \Delta\epsilon_{22}^*|$  is larger than  $|\Delta\epsilon_{33}^*|$  for **5** and **6**, their CD spectra are positive in the  $n-\pi^*$  region, whereas for compounds **1–4**  $|\Delta\epsilon_{11}^* + \Delta\epsilon_{22}^*|$  is smaller than  $|\Delta\epsilon_{33}^*|$  and thus their CD band is negative. Therefore, for the enones **1** to **4** the CD spectrum of the isotropic solution are mostly determined by  $\Delta\epsilon_{22}^*$ , and for enones **5** and **6** it is determined by  $(\Delta\epsilon_{11}^* + \Delta\epsilon_{22}^*)$ . This means that for **1–4** and for **5** and **6** the CD spectra are determined by the different views along the molecular frame, that is, views along the  $x_3^*$  or along an axis perpendicular to  $x_3^*$  of the “molecule rotating about  $x_3^*$ ”. Different helicities can be seen in both cases, and so different helicity rules should be given for  $\Delta\epsilon_{33}^*$  and for  $(\Delta\epsilon_{11}^* + \Delta\epsilon_{22}^*)$ , because the coordinates  $\Delta\epsilon_{ii}^*$  can have different signs when viewed along different directions of enone chromophores with the same torsion angles. Here, the negative sign of the torsion angle of the  $\Delta^4$ -6-oxo chromophore seems to correlate with the negative sign of  $\Delta\epsilon_{33}^*$ . For the last conclusion we assume that the enone chromophore of **1–6** is highly skewed also in the anisotropic phase as we have shown it recently for the crystalline state.<sup>[19]</sup>

Generalizing the conclusions it appears that for the assignment of the absolute configuration of a molecule, the CD of the same vibrational progressions has to be determined as has been used in the case of the reference molecule. Such a determination can be achieved with the help of ACD and polarized (LD) spectroscopy. The UV absorption of the  $n-\pi^*$  band is strongly influenced by the  $7\alpha$ -bromine substitution. The vibrational progression that is polarized perpendicularly to the orientation axis preferentially intensifies as a result of the degree of anisotropy for **5** and **6** (Figure 3) in comparison to the positive curves of **1–4**. The intensity change of the vibrational progressions in the UV spectra affects different  $\Delta\epsilon_{ii}^*$  in a diverse way as discussed above. The resulting sign change of the values of  $\Delta\epsilon$  without a corresponding change of helicity fits in the model given earlier.<sup>[10, 12]</sup>

With the same assumption for the order parameter determination as for the  $n-\pi^*$  transition, the analysis of  $\Delta\epsilon^A$  for the  $\pi-\pi^*$  transitions has been performed for  $\Delta\epsilon_{33}^*$  and  $(\Delta\epsilon_{11}^* + \Delta\epsilon_{22}^*)$  (Figures 5 and 6 and Table 3). For the  $\alpha$ -substituted compounds **1** and **3** the values of  $\Delta\epsilon_{33}^*$  as well as

Table 3. The sign of the tensor coordinates  $\Delta\epsilon_{ii}^*$  of the *cisoid* ketosteroids **1–6** in different wavelength [nm] regions.

	n- $\pi^*$ band		$\pi-\pi^*$ bands			
	sign $\Delta\epsilon_{33}^*$ (for the $\lambda$ region [nm])	sign $(\Delta\epsilon_{11}^* + \Delta\epsilon_{22}^*)$ (for the $\lambda$ region [nm])	(band I) sign $\Delta\epsilon_{33}^*$ (for the $\lambda$ region [nm])	sign $(\Delta\epsilon_{11}^* + \Delta\epsilon_{22}^*)$ (for the $\lambda$ region [nm])	(band II) sign $\Delta\epsilon_{33}^*$ (for the $\lambda$ region [nm])	sign $(\Delta\epsilon_{11}^* + \Delta\epsilon_{22}^*)$ (for the $\lambda$ region [nm])
<b>1</b>	– (400–294)	+ (400–333) <sup>[a]</sup> – (333–294)	+ (256–208)	+ (256–208)	+ (< 208)	+ (< 208)
<b>2</b>	– (400–294)	+ (400–339) <sup>[a]</sup>	+ (256–208)	– (256–213) – (213–208) <sup>[a]</sup>	+ (< 208)	+ (< 208)
<b>3</b>	– (400–294)	+ (400–345) <sup>[a]</sup> – (345–294) – (< 204) <sup>[a]</sup>	– (256–250) – (256–250) <sup>[a]</sup>	+ (256–208)	+ (208–204)	+ (< 208)
<b>4</b>	– (400–294)	+ (400–294) <sup>[a]</sup>	+ (238–208) + (256–208)	– (256–217) + (217–208) <sup>[a]</sup>	+ (< 208)	+ (< 208)
<b>5</b> <sup>[b]</sup>	– (400–313)	+ (400–294)	– (270–222) <sup>[a]</sup> + (222–217)	+ (270–217) – (217–208) <sup>[a]</sup>	+ (< 208)	+ (< 208)
<b>6</b> <sup>[b]</sup>	– (400–313)	+ (400–294)	+ (270–208)	+ (270–250) – (250–208)	+ (< 208)	– (< 208)

[a] Under the assumption  $S^* = R_{\max}$ . [b] There is no information about a preband.

( $\Delta\epsilon_{11}^* + \Delta\epsilon_{22}^*$ ) are positive, whereas for  $\beta$ -substituted compounds **2** and **4** the values of  $\Delta\epsilon_{33}^*$  are positive and ( $\Delta\epsilon_{11}^* + \Delta\epsilon_{22}^*$ ) are negative, independent of the kind of substituent (Figures 5 and 6, Table 3). As it was mentioned before in context of the ACD spectra, this may be a guide for a new stereochemical rule.

The effect of bromine substituent in compounds **5** and **6** yields complex ACD spectra. Therefore, further investigation is necessary before a discussion in more detail will be possible. The *cisoid* enone **7** is not analyzed here because of the large error for the  $\Delta\epsilon^A$  measurement and therefore it has been excluded from detailed discussion.

## Conclusion

The circular dichroism of isotropically distributed molecules, for example, isotropic solutions, expressed as  $\Delta\epsilon_{33}^*$  is one third of a sum of three independent coordinates  $\Delta\epsilon_{11}^*$ ,  $\Delta\epsilon_{22}^*$ , and  $\Delta\epsilon_{33}^*$ . From the experimental point of view each coordinate  $\Delta\epsilon_{11}^*$ ,  $\Delta\epsilon_{22}^*$ , and  $\Delta\epsilon_{33}^*$  is a CD measurement along one of three mutually orthogonal perpendicular directions with respect to the frame of a molecule. In the  $n-\pi^*$  spectral region  $\Delta\epsilon_{33}^*$  is negative for compounds **1–6**, whereas both signs and values of the sum ( $\Delta\epsilon_{11}^* + \Delta\epsilon_{22}^*$ ) are different within the series **1–6**. In particular, for **5** and **6** the ( $\Delta\epsilon_{11}^* + \Delta\epsilon_{22}^*$ ) values are positive and dominate in  $\Delta\epsilon$  so that the enone helicity rule is not allowed to be applied for the positive  $n-\pi^*$  Cotton effect (CE). For these compounds the vibrational progression that is polarized perpendicularly to the orientation axis—approximately the longest axis of the molecules—preferentially intensifies. Thus, the CD of **5** and **6** in the  $n-\pi^*$  region is determined by normal vibrations that do not contribute essentially to the CD of **1–4**. Therefore, for the correlation of the  $n-\pi^*$  CE sign and helicity of the  $\Delta^4$ -6-oxo chromophore in compounds **1–6**, values of  $\Delta\epsilon_{33}^*(\bar{\nu})$  should be taken in consideration instead of the usually applied  $\Delta\epsilon$ . Then the negative value of  $\Delta\epsilon_{33}^*(\bar{\nu})$  of the  $n-\pi^*$  CE corresponds to a positive ACD value ( $\Delta\epsilon^A$ ) of the  $\pi-\pi^*$  transition in band I spectral region.

From the result shown above a general conclusion is obtained in a context of the theory of vibronic coupling: the intensity of the  $n-\pi^*$  CD band of enone compounds is determined by contributions of at least two vibrational progressions of different sign. Insertion of substituents into these enones causes corresponding change of the ratio of their individual contributions so that there is a sign change of the CE without a change of the enone helicity. In those cases it is not possible to apply the helicity or sector rules because the measured CD in both investigated and reference compounds belongs to different vibrational transitions of the UV band of the chromophore. In other words, the rules can only be applied to the CD of molecules in which the main contribution of a CD band can be traced back to the same vibronic transitions, for example, to the same vibrational progression.

Therefore, ACD measurements are especially recommended for compounds of magnetically allowed, electrically forbidden dipole transition with small dissymmetry factor  $g = \Delta\epsilon/\epsilon$ .

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