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Optical Activity of Oriented Molecules. 5. α,β-Unsaturated Keto Steroids[1]

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Abstract: The CD ($\Delta\epsilon^{\Lambda}(\bar{\nu})$) of a transition Kk ← Nn of an anisotropic solution is determined by order coefficients g_{ij33}, the tensor of rotation $\mathbf{R}_{ij}^{\mathrm{NnKk}}$, and its frequency dependence $G_{(\bar{\nu})}^{\mathrm{NnKk}}$: $\Delta\epsilon^{\Lambda}(\bar{\nu}) = \sum_{i=1}^{3} \sum_{j=1}^{3} g_{ij33}\mathbf{R}_{ij}^{\mathrm{NnKk}}G_{(\bar{\nu})}^{\mathrm{NnKk}}$. For cholest-4-en-3-one, the 17β-substituted testosterones, 5α-androst-1-en-3-ones, and 5β-androst-1-en-3-ones oriented in a liquid crystal matrix (cholesteryl chloride/cholesteryl laurate) it is shown that the information from the CD of the anisotropic solution goes beyond that obtained from the isotropic CD. E.g., compounds which have nearly identical CD spectra in the isotropic state behave very differently in the oriented state. Furthermore, $\Delta\epsilon^{\Lambda}(\bar{\nu})$ depends on the 17β substitution. This can be explained by a variation of the order parameter as a function of the length of the substituent; i.e., for cholest-4-en-3-one and the testosterones the order increases in the succession -OH, -OCOCH$_3$, -OCOCH$_2$CH$_3$, -CH(CH$_3$)CH$_2$CH$_2$CH$_2$CH(CH$_3$)$_2$. The coordinates $R_{11}^{\mathrm{NK}} + R_{22}^{\mathrm{NK}}$ and R_{33}^{NK} of the tensor of rotation are estimated and an estimation of the contribution of the quadrupole transition moment is attempted.

I. Introduction

The circular dichroism (CD) and the optical rotatory dispersion (ORD) measurements in isotropic solutions turned out to be a very valuable method to determine the structure of molecules, especially the assignment of the absolute configuration and conformation.[2] The determination of the optical activity (CD, e.g.) of oriented molecules will be a precious completion of this method as will be shown by the analysis of the n-π* transition of several unsaturated keto steroids in this paper.

For a system of oriented molecules the circular dichroism $\Delta\epsilon^{\Lambda}(\bar{\nu})$ for a transition from the ground state Nn to the excited state Kk is proportional to $R_{\alpha\alpha}^{\mathrm{NnKk}}$[3,4] if the light propagates parallel to the axis x_α ($\alpha = 1, 2, 3$; $x_1 = x$; $x_2 = y$; $x_3 = z$) as shown in Figure 1. Therefore three independent numbers, R_{11}^{NnKk}, R_{22}^{NnKk}, and R_{33}^{NnKk}, exist which determine the CD of the compound. The sum of these three coordinates

$$R^{\mathrm{NnKk}} = R_{11}^{\mathrm{NnKk}} + R_{22}^{\mathrm{NnKk}} + R_{33}^{\mathrm{NnKk}} \qquad (1)$$

represents the usual rotational strength R^{NnKk} for the transition Kk ← Nn, which is theoretically defined by a scalar product of an electric and magnetic dipole transition moment. The coordinates $R_{\alpha\alpha}^{\mathrm{NnKk}}$ are also determined by the components of this scalar product and additionally by a product of an electric dipole and an electric quadrupole transition moment (eq 7).[4,5] Because of the independence of these three coordinates $R_{\alpha\alpha}^{\mathrm{NnKk}}$ ($\alpha = 1, 2, 3$), three independent pieces of structural information should be available. These three pieces of information can be understood as projections of the information "chirality" on three planes perpendicular to the direction of the propagation of light with which the CD or ORD is measured (Figure 1). This conclusion can easily be seen if only the electric and magnetic dipole contributions are considered (eq 7). Therefore one can expect that for two compounds which cannot be distinguished in their chirality because of an equal CD or rotational strength of the isotropical solution, the various coordinates $R_{\alpha\alpha}^{\mathrm{NnKk}}$ should be different.

If we assume that the transition between the states Kk ← Nn (N and K indicate the electronic ground and excited state,

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respectively; n and k describe the vibrational state in N and K, respectively) is connected with a CD band, which has the frequency dependence $G_{(\bar{\nu})}^{\text{NnKk}}$, then $\Delta\epsilon^{\wedge}(\bar{\nu})$ is proportional to $R_{\alpha\alpha}^{\text{NnKk}}G_{(\bar{\nu})}^{\text{NnKk}}$ and $\Sigma_{\text{n}}\Sigma_{\text{Kk}}R_{\alpha\alpha}^{\text{NnKk}}G_{(\bar{\nu})}^{\text{NnKk}}$, respectively, if superpositions of different transitions Kk ← Nn occur.

Usually one cannot orient molecules completely and one has to take account of an incomplete orientation. This can be done by six different orientational distribution coefficients g_{ij33} which are a special form of order parameters.[6] Then the CD of an anisotropic solution can be described by[5]

$$\Delta\epsilon^{\wedge}(\bar{\nu}) = B\bar{\nu}\sum_{i=1}^{3}\sum_{j=1}^{3} g_{ij33}\sum_{\text{n}}\sum_{\text{Kk}} \mathbf{R}_{ij}^{\text{NnKk}}G_{(\bar{\nu})}^{\text{NnKk}}$$

$$B = \frac{32\pi^3 N_{\text{L}}}{10^3 hc \ln 10} \qquad (2)$$

N_{L} is Avogadro's number, $\bar{\nu}$ is the wavenumber (cm^{-1}), h is Planck's constant, and c is the velocity of light in the vacuum. From eq 2 the contribution of an electronic transition K ← N can be calculated by integration over the area of the CD band:

$$R^{\text{T}} = \sum_i\sum_j g_{ij33}\mathbf{R}_{ij}^{\text{NK}} = \frac{1}{B}\int\frac{\Delta\epsilon^{\wedge}(\bar{\nu})}{\bar{\nu}}\,\text{d}\bar{\nu} = \frac{22.9_6 \times 10^{-40}}{3}\int\frac{\Delta\epsilon^{\wedge}(\bar{\nu})}{\bar{\nu}}\,\text{d}\bar{\nu}\ [\text{cgs}] \qquad (3)$$

In analogy to the rotational strength R, which can be obtained from eq 3 by using

$$g_{ij33} = \frac{1}{3}\delta_{ij}\left(\delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases}\right)$$

we have named R^{T} as the tensorial rotational strength.

From eq 2 one can see that the measured effect is built up by a sum of products of two quite different terms. One of them determines the chirality of the system ($\mathbf{R}_{ij}^{\text{NnKk}}$ tensor of rotation). The other one depends only on the type and extent of orientation of the molecules and is therefore determined by the degree of order of the system. For the structural information the last term is only of secondary meaning, but it has to be known in order to obtain the chirality of the system. Because the orientational distribution function is only known for some special systems, the calculation of the coefficients g_{ij33} is generally not possible. The experimental determination, from UV or NMR data, e.g., is uncertain and affected with large errors, respectively. To avoid this problem one can measure the CD of different molecules under conditions where the orientation and the order parameter are nearly the same. Then the measured $\Delta\epsilon^{\wedge}(\bar{\nu})$ themselves can be used on the whole for the structural analysis. But this condition has to be examined very carefully, because a change in the order parameter can have a large effect on $\Delta\epsilon^{\wedge}(\bar{\nu})$ as shown in the preceding paper.[5]

II. Experimental Section

1. Method. The optically active compounds were solved in a mixture of cholesteryl chloride/cholesteryl laurate (1.8:1 by weight). The mixture has a nematic phase about $T_{\text{nem}} \approx 36$ °C,[7a,8] which is somewhat dependent on the concentration of the solute. The sample can be oriented by a dc electric field with a field strength in the order of 2×10^6 V/m.[10] Under this condition the sample is completely transparent.

The CD is measured with a light beam propagating parallel to the orienting electric field. In this case the linear dichroism and linear birefringence are zero by symmetry, because the light propagates parallel to the optical axis of the system. In order to minimize errors, produced by remaining linear dichroism which may be generated by filling the cuvette, e.g., the measurements are done in six different positions, which one gets by rotating the sample around the direction of the propagation of light. Pairs of these positions always differ by an angle of 90°, because under this condition the linear dichroism has opposite sign and therefore can be eliminated by calculating the mean value.

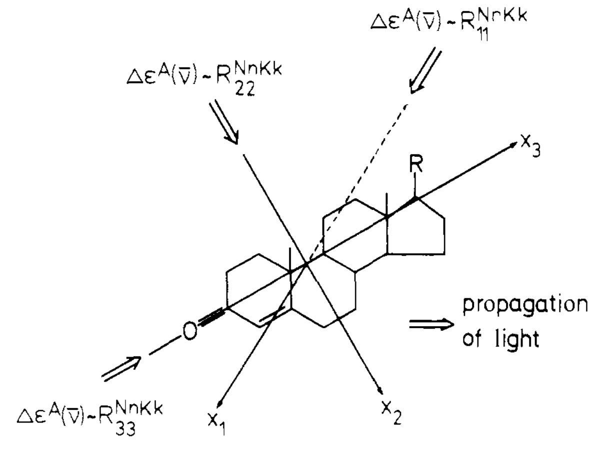

Figure 1. CD measured with light beams propagating in different directions with respect to the molecule and its relation to the coordinates of the tensor of rotation $\mathbf{R}_{ij}^{\text{NnKk}}$.

The filling of the cuvette has to be done very carefully in order to avoid linear dichroism. For this a special cuvette was developed.[11] Furthermore, the chemical stability of the solution was examined by measuring the CD of the isotropic sample before and after the measurement of the anisotropic system was done.

The CD was measured with the Cary 60 and the dichrograph III of CNRS/Roussel/Jouan, and the anisotropic absorption with the Cary 17 in a special cell and cell holder.[12] The CD and UV spectra in the organic solvents were determined at room temperature (~23 °C), and those in the isotropic state of the liquid crystal mixture at 80 °C. While the measurement of the CD spectra in the oriented mesophase was performed at 35.3 °C, the UV spectra and therefore the degree of polarization was obtained at 38.2 °C.

2. Materials. Cholesteryl chloride (Merck/Darmstadt) was refined by chromatography on silica gel with cyclohexane/chloroform (4:1) and following recrystallizations from ethanol/dioxane (9:1), and **cholesteryl laurate** (Merck/Darmstadt) was recrystallized from methanol/dioxane (2:1). **3β-Acetoxycholest-5-en-7-one**[13] **(2)** was recrystallized from petroleum ether. **Cholest-4-en-3-one (1)** (Roth/Karlsruhe) was purified by recrystallization from ethanol. **Testosterone** (17β-hydroxyandrost-4-en-3-one) **(3)** (EGA-Chemie) and **testosterone propionate (5)** (Fluka AG) were used without further purification. **Testosterone acetate (4)** (Fluka AG) was recrystallized from isooctane. **17β-Hydroxy-5α-androst-1-en-3-one**[14] **(6)** was refined by thin layer chromatography on silica gel with ether/cyclohexane (5:1) and following recrystallization from *n*-hexane. **17β-Acetoxy-5α-androst-1-en-3-one (7)** was sufficiently pure, while **17β-propionyloxy-5α-androst-1-en-3-one (8)** was purified by thin layer chromatography on silica gel with cyclohexane/acetone (3:1) and then recrystallized from ethanol. **17β-Hydroxy-5β-androst-1-en-3-one (9)** and **17β-acetoxy-5β-androst-1-en-3-one (10)** were used without further purification. **17β-Propionyloxy-5β-androst-1-en-3-one (11)** was synthesized from **9** and propionic anhydride and refined by thin layer chromatography on silica gel with cyclohexane/acetone (3:1).

III. Results and Discussion

Four different types of α,β-unsaturated keto steroids were selected for the measurement of the anisotropy of the optical activity (Figure 2).

1. UV and CD Spectra of the n-π* Transition of the Isotropic Solution. Within the series A (**1, 3, 4, 5**) the CD and UV spectra are very similar (Figures 4, 5, 6, 7, and 14). Only the UV spectra of **1** and the CD ($\Delta\epsilon_{\text{iso}}$) of **1** and **3** in the isotropic solution of cholesteryl chloride/cholesteryl laurate deviate more than the other from the mean value calculated for this series (Table I). Nevertheless the substituent at the 17β position has only a small or no influence on the chromophoric group as also can be seen from the data given in Table I. The same conclusion holds for the 5α-androstenones (**6, 7, 8,** Figures 8, 9, 10, and 15, Table I) and the 5β-androstenones (**9, 10, 11,**

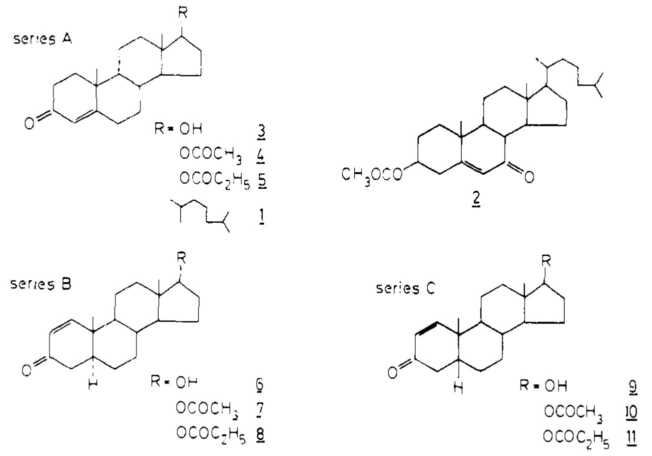

Figure 2. Molecular structures of the α,β-unsaturated keto steroids studied.

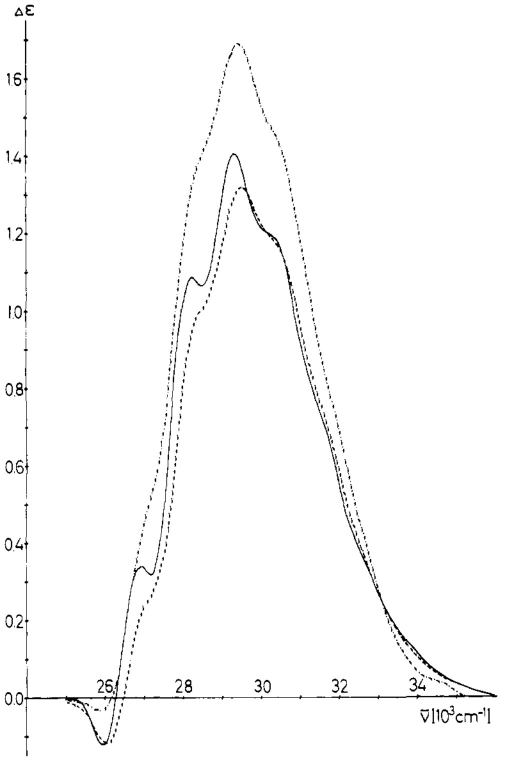

Figure 3. CD spectra of 3β-acetoxyandrost-5-en-7-one (**2**) in *n*-heptane (—), in the liquid crystal mixture in the isotropic state (- - -), and in the oriented state (- · · · · -).

Figures 11, 12, 13, and 16, Table I). Within these two series the CD and UV spectra of the particular molecules differ more among one another than those of series A. But a systematic change as a function of the length of the substituent in the 17β position cannot be seen. The larger changes in the bisignated CD curve within the series C seem to be a hint for a special behavior which can also be seen in the solvent or temperature dependence where with increasing polarity of the solvent or decreasing temperature a shift to a more positive CD occurs.[2,3] This may indicate a conformational change produced by different solvation of the molecules **9**, **10**, or **11** influenced by their different substitution in the 17β position. But the similarity of the UV and CD bands within all series examined here is in agreement with the long-known fact that a substitution far away from the chromophore does not influence the CD spectra very much.

In all the molecules studied here, the enone group is the essential chromophore for the CD and UV spectra discussed. Comparison of the CD and UV spectra of the different series therefore should give some information about the structure of the enone group in these series. The molecules of the series A and B have very similar CD and UV curves. The spectra of **6–8** are 20–25% smaller than those of **1**, **3**, **4**, and **5**. Furthermore, the vibrational structure of the CD curves of **6–8** is somewhat higher than that of **1**, **3**, **4**, and **5** especially in the high-frequency region of the n-π* transition. From this similarity one may conclude that the enone group in both series has the same arrangement. As will be shown in the following chapters, this conclusion is not correct. The same question arises when the CD spectra of **1** and **2** are compared. Here Djerassi and coworkers concluded from the ORD spectra in isotropic solutions that the chromophoric systems are mirror images.[15] The bi-

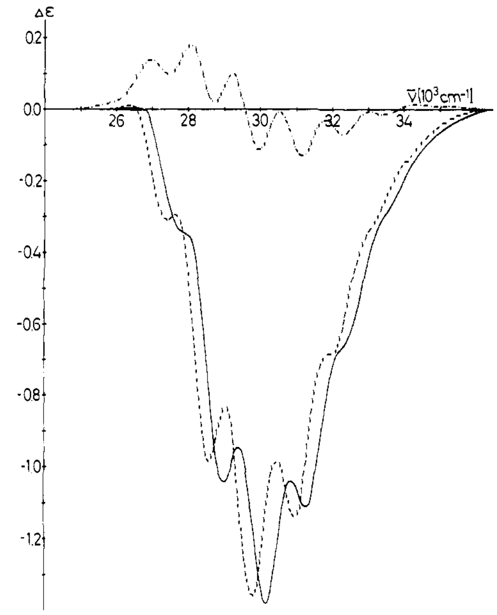

Figure 4. CD spectra of testosterone (**3**) in dioxane (—), in the liquid crystal mixture in the isotropic state (- - -), and in the oriented state (- · · · -).

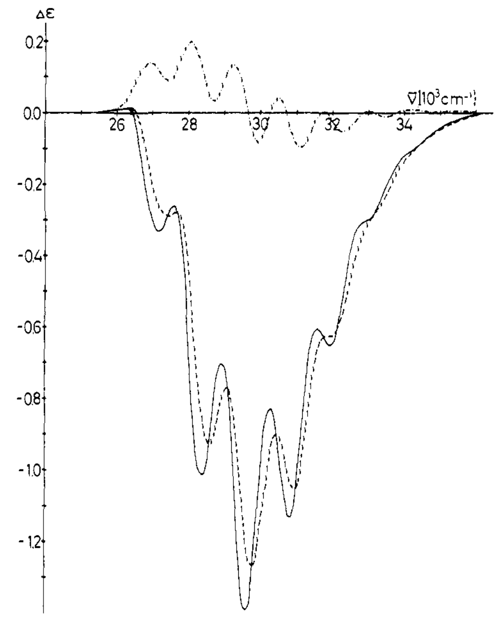

Figure 5. CD spectra of testosterone acetate (**4**) in *n*-heptane (- -), in the liquid crystal mixture in the isotropic state (- - -), and in the oriented state (- · · · -).

Table I. Characteristic Data of the α,β-Unsaturated Keto Steroids **1-11**

compd	$R^{T}\times 10^{40\ h,i}$	$R_{iso}\times 10^{40\ h}$	$R\times 10^{40\ a,h}$	$D_{iso}\times 10^{38\ g,h}$	$D\times 10^{38\ a,g,h}$	$\Delta e^{A}\ (\bar{\nu}_{max})^{f,i}$	$\Delta\epsilon_{iso}\ (\bar{\nu}_{max})^{e,f}$	$\Delta\epsilon(\bar{\nu}_{max})^{a,f}$	$\epsilon_{iso}(\bar{\nu}_{max})^{e,f}$	$\epsilon(\bar{\nu}_{max})^{a,f}$
2	1.77	4.17	4.26	5.25	4.88	1.69 (29.4)	1.37 (29.4)	1.34 (29.4)	33.4 (29.8)	30.9 (29.7)
1	0.44	−3.75	−3.94	6.62	5.76	0.44 (28.3)	−1.39 (29.8)	−1.44 (29.6)	46.2 (30.0)	40.4 (29.8)
3	0.05	−3.86	−3.71^{b}	6.64	6.59^{b}	0.18 (28.1)^{d}	−1.36 (29.7)	−1.38 (30.2)^{c}	41.1 (30.0)	40.4 (29.7)^{b}
			−3.93^{c}		7.00^{c}	−0.13 (31.2)				46.6 (30.2)^{c}
4	0.14	−3.59	−3.80	5.58	5.69	0.23 (28.1)^{d}	−1.27 (29.7)	−1.42 (29.5)	38.6 (29.9)	38.7 (29.6)
						−0.06 (31.2)				
5	0.18	−3.61	−3.74	5.83	5.71	0.26 (28.2)^{d}	−1.28 (29.9)	−1.40 (29.5)	40.4 (29.9)	38.5 (29.6)
					−0.03 (31.2)					
6	−0.88	−2.82	−2.32	5.31	4.14	−0.98 (28.8)	−1.03 (28.7)	−0.96 (28.6)	27.8 (29.9)	24.3 (29.1)
7	−1.09	−3.21	−2.76	4.33	4.33	−1.05 (28.8)	−1.10 (28.7)	−1.05 (28.6)	27.2 (29.2)	26.3 (29.1)
8	−1.14	−2.43	−1.73	5.07	4.98	−1.00 (28.9)	−0.86 (28.9)	−0.76 (28.7)	28.9 (29.3)	28.5 (29.0)
9^{d}	0.08	0.43	0.51^{c}	4.91	4.53^{c}	0.16 (26.4)	0.33 (27.7)	0.35 (28.1)^{c}	28.2 (30.3)	28.9 (30.2)^{c}
	−0.24	−0.45	−0.36^{c}			−0.34 (29.7)	−0.24 (30.9)	−0.18 (31.3)^{c}		
10^{d}	0.02	0.37	0.41	4.08	3.94	0.08 (26.2)	0.31 (27.7)	0.39 (27.5)		
	−0.58	−0.65	−0.46			−0.65 (29.6)		[−0.27 (29.5)]	25.8 (29.6)	24.5 (29.3)
							−0.30 (30.8)	−0.26 (30.7)		
11^{d}	0.01	0.32	0.44			0.06 (26.2)	0.28 (27.7)	0.38 (27.6)		
	−0.69			4.23	4.02		[−0.32 (29.6)]	[−0.28 (29.5)]	26.2 (29.5)	25.1 (29.2)
		−0.72	−0.48			−0.73 (29.6)	−0.31 (30.8)	−0.26 (30.7)		

[a] *n*-Heptane, if not stated otherwise. [b] Cyclohexane. [d] Dioxane. [d] Bisignated CD curve. [e] Mixture of cholesteryl chloride and cholesteryl laurate (1.8:1 by weight) in the isotropic state (t = 80 °C). [f] $\bar{\nu}[10^3\ \mathrm{cm}^{-1}]$. [g] A systematic error by a small contribution of an overlapping band at higher wavelength is contained in these data. [h] Dipole strength $D = 91.8\times 10^{-40}\int(\epsilon(\bar{\nu})/\bar{\nu})\mathrm{d}\bar{\nu}$ [cgs]; R^{T}, R_{iso}, R [cgs]. [i] These values depend on concentration; for the A series c was chosen ~4-7 × 10^{-2}, for the B series c ~ 5-7 × 10^{-2}, for the C series c ~ 3-4 × 10^{-2} mol/L.

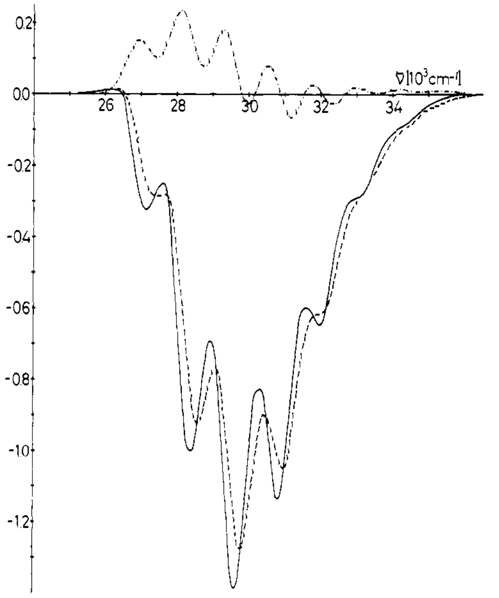

Figure 6. CD spectra of testosterone propionate (**5**) in *n*-heptane (—), in the liquid crystal mixture in the isotropic state (- - -), and in the oriented state (- · · · · -).

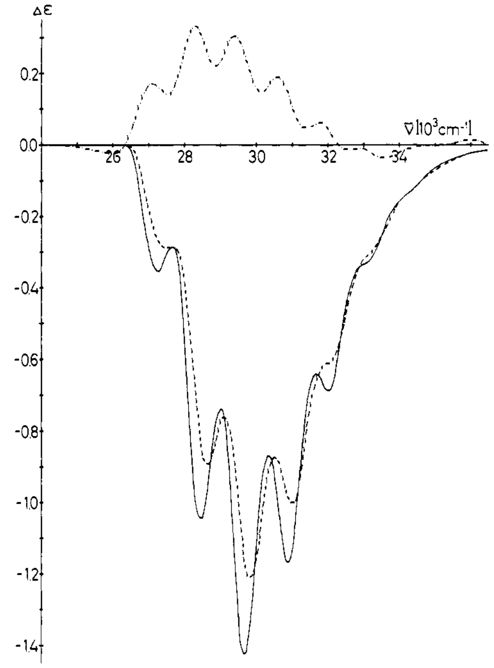

Figure 7. CD spectra of cholest-4-en-3-one (**1**) in *n*-heptane (—), in the liquid crystal mixture in the isotropic state (- - -), and in the oriented state (- · · · -).

signated CD curves of the 5β-androst-1-en-3-ones behave very different from that of the series A and B. This may be due to vibronic coupling as described by Weigang et al.[16] or to a superposition of CD curves of different conformers as discussed before.

In order to compare the spectra of the anisotropic solution with those of the isotropic solution one has to raise the question whether the mixture cholesteryl chloride/cholesteryl laurate, used as a solvent here, causes any special effects on the compounds. In the isotropic state of this solution the CD and UV spectra are very similar to those measured in organic solvents as *n*-heptane and dioxane (Figure 3-16). The vibronic structure measured in the mixture is stronger than in dioxane but smaller than or equal to that in *n*-heptane. The position of the bands is shifted to higher and smaller wavenumbers if compared with *n*-heptane and dioxane, respectively. Roughly spoken it seems that the mixture behaves in the isotropic state as a normal organic solvent located between *n*-heptane and dioxane.

2. UV and CD Spectra of the Anisotropic Solutions. a. Qualitative Discussion. The molecules are solved in the oriented

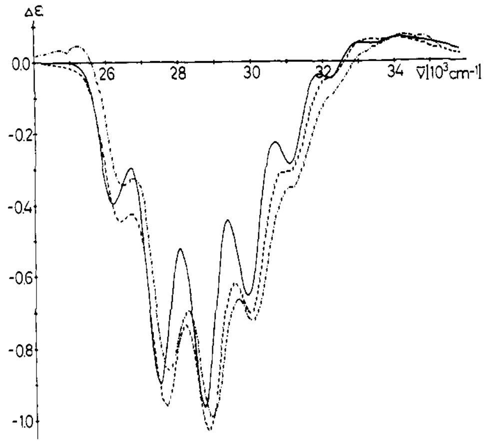

Figure 8. CD spectra of 17β-hydroxy-5α-androst-1-en-3-one (**6**) in *n*-heptane (—), in the liquid crystal mixture in the isotropic state (- - -), and in the oriented state (- · - · -).

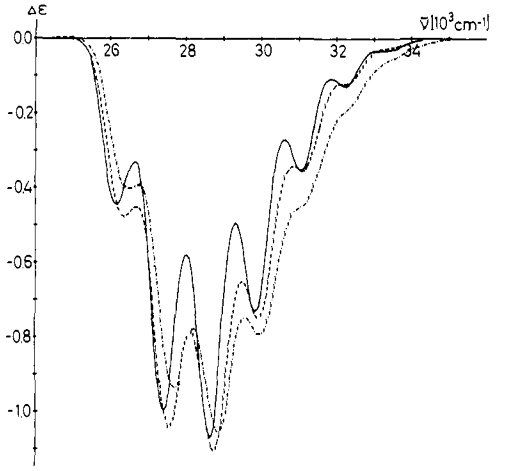

Figure 9. CD spectra of 17β-acetoxy-5α-androst-1-en-3-one (**7**) in *n*-heptane (—), in the liquid crystal mixture in the isotropic state (- - -), and in the oriented state (- · - · -).

compensated nematic phase consisting of cholesteryl chloride/cholesteryl laurate. The extent of the orientation can be seen from the magnitude of the degree of polarization $P = (\epsilon_1 - \epsilon_2)/(\epsilon_1 + \epsilon_2)$ where ϵ_1 and ϵ_2 are the absorption coefficients for the light polarized parallel and perpendicular, respectively, to the orienting electric field. For each series A, B, and C (see Figure 2) one example of the degree of polarization is given in Figures 14–16. The results of **2** have been discussed earlier.[4,17] For the 5β-androstenones the degree of polarization is about zero. But certainly this does not mean that there is no orientation, because all other compounds of similar structure are oriented to a large extent. In this case it is more probable that the direction of the transition moment is about 54.7° with respect to the x_3 axis of the molecule (Figure 1), where the degree of polarization is zero.

The orientation axes and the x_3 axis of the molecules as examined here are not easily defined with respect to the molecular skeleton, because no symmetry exists. Using the model of Sackmann et al.[18] the orientation will be determined by the anisotropy of the polarizabilities $2\alpha_{33} - \alpha_{22} - \alpha_{11}$ or by differences of the molecular lengths $2l_{33} - l_{22} - l_{11}$. From this model we may assume that the solute molecules are mainly oriented parallel with their long molecular axis (x_3 axis) to the orienting field. Therefore, for our experimental condition, $\Delta\epsilon^{\Lambda}(\bar{\nu})$ can be interpreted as a sum of two CD measurements. One of them is the measurement with light propagating parallel to the x_3 axis of the molecules ($\Delta\epsilon_{33}^{\Lambda}(\bar{\nu})$; see also Figure 1). The second one is the CD of the isotropic solution.

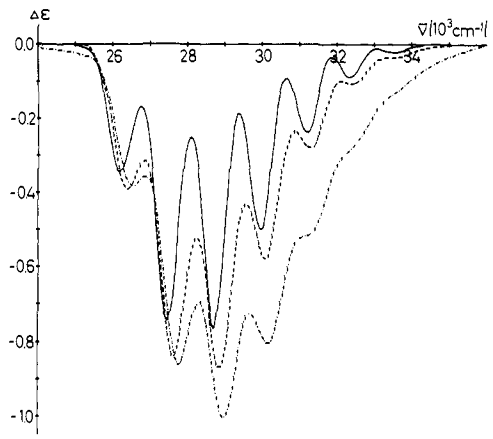

Figure 10. CD spectra of 17β-propionyloxy-5α-androst-1-en-3-one (**8**) in *n*-heptane (—), in the liquid crystal mixture in the isotropic state (- - -), and in the oriented state (- · - · -).

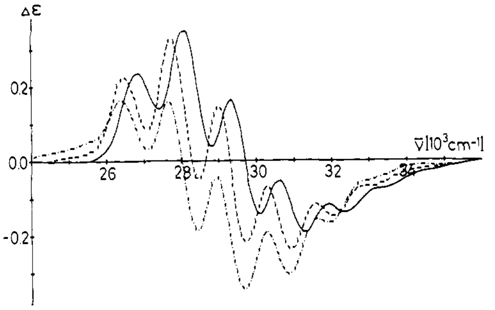

Figure 11. CD spectra of 17β-hydroxy-5β-androst-1-en-3-one (**9**) in dioxane (—), in the liquid crystal mixture in the isotropic state (- · -), and in the oriented state (- · - · -).

$\Delta\epsilon^{\Lambda}(\bar{\nu})$ (Figures 3–13) or the R^{T}'s (Table I) of the molecules studied exhibit a very different behavior. In spite of the fact that the series A (**1**, **3**, **4**, and **5**) and B (**6**, **7**, and **8**) have a very similar negative CD in the isotropic solution, the anisotropic CD ($\Delta\epsilon^{\Lambda}(\bar{\nu})$) changes its sign or has a bisignated curvature for series A, while there is only a very small or no change in the CD for series B. For **2** an enhancement of the positive CD curve takes place. The bisignated curve in the isotropic solution for series C changes within the series to a strong negative CD in the oriented state.

From this we can see that in addition to the information from isotropic solutions a further differentiation between different but similar molecules from the anisotropic CD can be obtained.

Within the series A and C a variation of $\Delta\epsilon^{\Lambda}(\bar{\nu})$ depending on the length of the chain in the 17β position can be seen. The bisignated curve of **3** changes more and more to a positive curve in the sequence **3**, **4**, **5**, and **1**. In the same way $\Delta\epsilon^{\Lambda}(\bar{\nu})$ of the 5β-androstenones changes from the bisignated curve of **9** to a nearly negative band for **11**. For the explanation of this behavior, two alternative interpretations are possible if one excludes conformational changes due to the effect of the oriented liquid crystal matrix.[5] The first one starts from the concentration dependence of $\Delta\epsilon^{\Lambda}(\bar{\nu})$ found for this type of molecules and analyzed especially for **5**.[5] Here a variation occurs by the change in the order parameter ρ described by

$$\Delta\epsilon^{\Lambda}(\bar{\nu}) = (1 - \rho)\Delta\epsilon_{\mathrm{iso}}(\bar{\nu}) + \rho\Delta\epsilon_{33}^{\Lambda}(\bar{\nu}) \qquad (4)^{19}$$

$\Delta\epsilon_{\mathrm{iso}}(\bar{\nu}) = (\Delta\epsilon_{11}^{\Lambda}(\bar{\nu}) + \Delta\epsilon_{22}^{\Lambda}(\bar{\nu}) + \Delta\epsilon_{33}^{\Lambda}(\bar{\nu}))/3$. $\Delta\epsilon_{\alpha\alpha} = B\bar{\nu}\,\Sigma_{\mathrm{n}}\,\Sigma_{\mathrm{Kk}}R_{\alpha\alpha}^{\mathrm{NnKk}} \cdot G_{(\bar{\nu})}^{\mathrm{NnKk}}$ ρ describes the amount of the molecules oriented; its value is one for a complete order and zero for the isotropic solution. Because ρ depends—as also known from, e.g., NMR

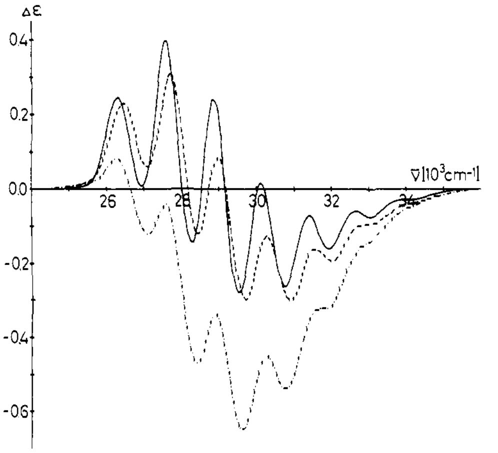

Figure 12. CD spectra of 17β-acetoxy-5β-androst-1-en-3-one (**10**) in *n*-heptane (—), in the liquid crystal mixture in the isotropic state (- - -), and in the oriented state (- · · · -).

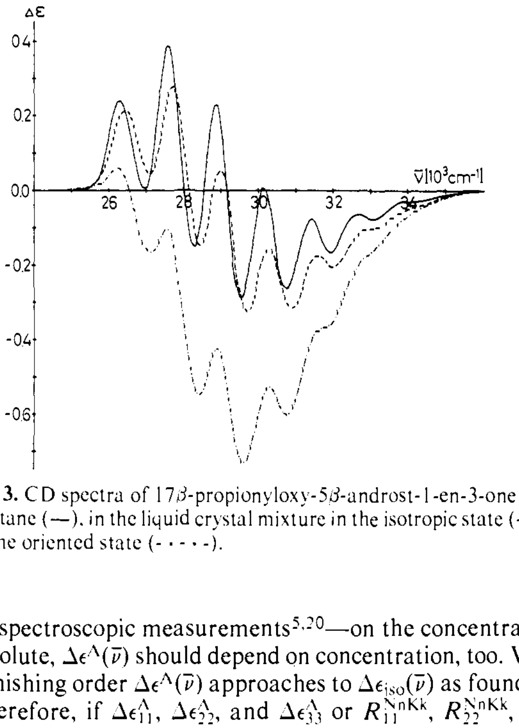

Figure 13. CD spectra of 17β-propionyloxy-5β-androst-1-en-3-one (**11**) in *n*-heptane (—), in the liquid crystal mixture in the isotropic state (- - -), and in the oriented state (- · · · -).

or UV spectroscopic measurements[5,20]—on the concentration of the solute, $\Delta\epsilon^{\Lambda}(\bar{\nu})$ should depend on concentration, too. With a diminishing order $\Delta\epsilon^{\Lambda}(\bar{\nu})$ approaches to $\Delta\epsilon_{\mathrm{iso}}(\bar{\nu})$ as found for **5**.[5] Therefore, if $\Delta\epsilon_{11}^{\Lambda}$, $\Delta\epsilon_{22}^{\Lambda}$, and $\Delta\epsilon_{33}^{\Lambda}$ or R_{11}^{NnKk}, R_{22}^{NnKk}, and R_{33}^{NnKk} for the molecules within one series are the same, the variation of the CD originates from the change of order.

The alternative interpretation arises from a rotation of the molecular framework with respect to the direction of propagation of light. As a consequence of this the coordinates of the tensor of rotation $\mathbf{R}_{ij}^{\mathrm{NnKk}}$ with respect to the direction of the propagation of light would change and the measured effect is then determined by $R_{33}^{\prime\mathrm{NnKk}}$ instead of R_{33}^{NnKk}. $R_{33}^{\prime\mathrm{NnKk}}$ can then be calculated by a tensor transformation. In general

$$R_{33}^{\prime\mathrm{NnKk}} = f(R_{11}^{\mathrm{NnKk}}, R_{22}^{\mathrm{NnKk}}, R_{33}^{\mathrm{NnKk}}) \tag{5a}$$

and

$$\Delta\epsilon^{\prime\Lambda}(\bar{\nu}) = f(\Delta\epsilon_{11}^{\Lambda}, \Delta\epsilon_{22}^{\Lambda}, \Delta\epsilon_{33}^{\Lambda}) \tag{5b}$$

One can say that $R_{33}^{\prime NnKk}$ and R_{33}^{NnKk} are different, because the light "sees" the molecule from another direction. The rotation of the molecule with respect to the direction of the propagation of the light wave or—having the same meaning—the change of the direction of the longest molecular axis could be caused by a different substitution in the 17β position.

How can one distinguish between these two models? Theoretically it can be shown that the frequency dependence of $\Delta\epsilon^{\Lambda}(\bar{\nu})$ as a function of the length of the chain should be different in both cases. If the first model were responsible for the effect, the concentration dependence should lead to the same change in the band structure as the variation of the substituent, if we assume that the chromophore is not affected by this 17β substitution. At the moment an unequivocal decision between both models cannot be given. But there seems to be good justifications to explain the experimental results by a change of order due to the substitution. In the following section it will be shown that we have to assume for the series A an increasing order in the succession -OH, $-OCOCH_3$, $-OCOCH_2CH_3$, and $-CH(CH_3)CH_2CH_2CH_2CH(CH_3)_2$. The small deviations in the frequency dependence of $\Delta\epsilon^{\Lambda}(\bar{\nu})$ of **1** compared with the frequency dependence of $\Delta\epsilon^{\Lambda}(\bar{\nu})$ as a function of concentration may be a hint that the second model also contributes to the effect. But the deviation in the $\Delta\epsilon^{\Lambda}(\bar{\nu})$ curves is so small that further experimental results—which are in progress—are necessary for a good analysis.

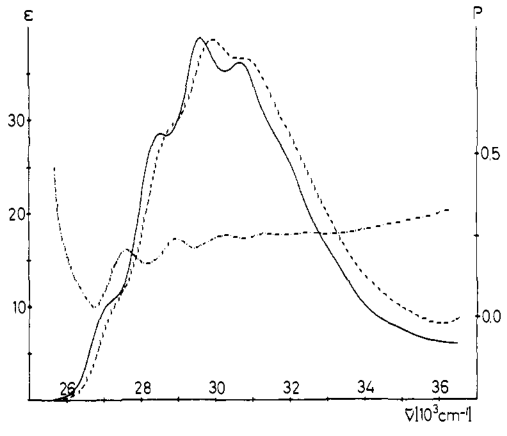

Figure 14. UV spectra of testosterone acetate (**4**) in *n*-heptane (—), in the liquid crystal mixture in the isotropic state (- - -), and the degree of polarization (- · · · -).

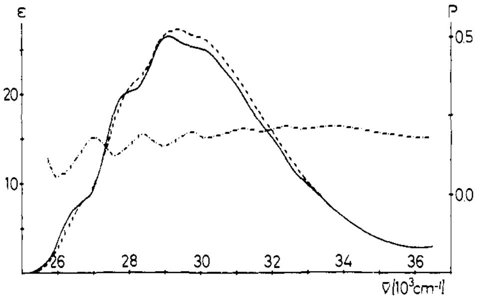

Figure 15. UV spectra of 17β-acetoxy-5α-androst-1-en-3-one (**7**) in *n*-heptane (—), in the liquid crystal mixture in the isotropic state (- - -), and the degree of polarization (- · · · -).

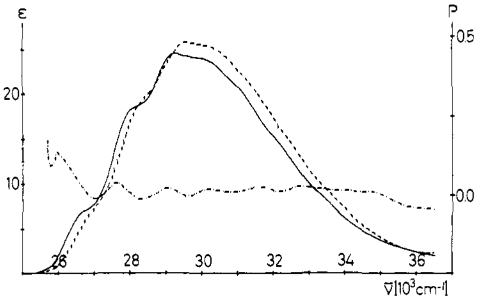

Figure 16. UV spectra of 17β-acetoxy-5β-androst-1-en-3-one (**10**) in *n*-heptane (—), in the liquid crystal mixture in the isotropic state (- - -), and the degree of polarization (- · · · -).

Table II. Coordinates of the Tensor of Rotation Calculated from Equation 6a

compd	$(R_{11}^{NK} + R_{22}^{NK})/R_{iso}^{NK}$	R_{33}^{NK}/R_{iso}^{NK}	$(R_{11}^{NK} + R_{22}^{NK}) \times 10^{40}$, cgs	$R_{33}^{NK} \times 10^{40}$, cgs
2	0.33	0.67	1.4	2.8
3	1.95 (2.11)	−0.95 (−1.11)	−7.5 (−8.1)	3.7 (4.3)
4	2.05 (2.10)	−1.05 (−1.10)	−7.3 (−7.5)	3.8 (3.9)
5	2.09 (2.09)	−1.09 (−1.09)	−7.5 (−7.5)	3.9 (3.9)
1	2.34 (2.08)	−1.34 (−1.08)	−8.8 (−7.8)	5.0 (4.0)
6	0.75	0.25	−2.1	−0.7
7	0.64	0.36	−2.1	−1.1
8	0.16	0.84	−0.4	−2.03
9	−27.7	28.7	0.6	−0.6
10	−5.51	6.51	1.5	−1.8
11	−4.40	5.40	1.8	−2.2

Table III. Mean Values of the Coordinates of the Tensor of Rotation

series	compds	$(R_{11}^{NK} + R_{22}^{NK}) \times 10^{40}$, cgs	$R_{33}^{NK} \times 10^{40}$, cgs	$R_{iso}^{NK} \times 10^{40}$, cgs
	2	1.4	2.8	3.2
A	**1, 3, 4, 5**	−7.7	4.0	−3.7
B	**6, 7, (8)**	−2.1	−0.9	−3.0
C	**(9), 10, 11**	1.7	−2.0	−0.3

b. Quantitative Analysis of the CD. If in the first analysis the band structure of the electronic transition K ← N is renounced, one can calculate the coordinates of the tensor of rotation $R_{11}^{NK} + R_{22}^{NK}$ and R_{33}^{NK} from the tensorial rotational strength R^T by eq 6, which is derived from eq 3 and 4:

$$R^T = \frac{1}{3}(1 - \rho)R_{iso}^{NK} + \rho R_{33}^{NK} \qquad (6a)$$

$$R_{iso}^{NK} = R_{11}^{NK} + R_{22}^{NK} + R_{33}^{NK} \qquad (6b)^{21}$$

For this calculation ρ has to be known. In a first approximation one can assume a constant value of ρ for all compounds. Thereby a value of $\rho = 0.27$ has been evaluated assuming that the compounds **2**, **5**, and **8** are equally oriented.[5] This approximation is in contrast to the model for the substituent dependence discussed in section 2a. But this dependence is relatively small and one can hope to get a good reference point for further discussions because the skeletons of the molecules of the series A and B are very similar. Since the A/B ring junction within the series C is cis, the ρ value can only be seen as a relative reference point.

In order to avoid errors introduced by differences in the optical purity, the relative tensor coordinates $R_{\alpha\alpha}^{NK}/R_{iso}^{NK}(\alpha = 1, 2, 3)$ are calculated, too.

While the chromophore is the same for all molecules within the series A, B, and C, one would expect comparable values for $R_{11}^{NK} + R_{22}^{NK}$ and R_{33}^{NK} for each series. As one can see in Table II, the relative coordinates and the coordinates of the tensor of rotation are of the same order of magnitude within the three series A, B, and C. The deviation of **8** seems to have its origin in the very different rotational strength of the isotropic solution (Table I) which cannot be explained at the moment. The difference of **9** with respect to **10** and **11** should be due to an experimental error because of the very small values of R^T and R_{iso}^{NK} (∼−0.2 and −0.02, Table I) which in this case are a sum of a large positive and negative number.

In the series A a small increase of the relative tensor coordinates in sequence **3**, **4**, **5**, and **1** as well as a decrease in series C for **10** and **11** is to be seen. This seems to be due to the neglect of the influence of the substitution in the 17β position, also to be seen directly in the CD spectra. Using the assumption that this small change originates from neglecting the variation of the order parameter as a function of the 17β substituent (first mechanism in section 2a) new order parameters can be estimated. For that the experimental curves of **1**, **3**, and **4** are compared with the functions $\Delta\epsilon^A(\bar{\nu},\rho)$ as derived for **5** in the preceding paper.[5] Here $\rho = 0.27$ is used as the reference point. For the series A an increase of ρ in the sequence **3** ($\rho = 0.24$), **4** (0.26), **5** (0.27), and **1** (0.32) occurs. The longer the chain of the 17β substituent is, the larger the order will be. This is in agreement with the model given by Sackmann et al.[18] The recalculated tensor coordinates are represented in Table II in brackets behind the numbers calculated with $\rho = 0.27$. Here the dependence on the length of the chain is lost within the experimental error. For the 5α-androstenones (series B) no dependence of ρ can be developed. This can also be seen from the CD curves $\Delta\epsilon^A(\bar{\nu})$ (Figures 8–10), which are nearly equal to $\Delta\epsilon_{iso}(\bar{\nu})$. In the 5$\beta$-androstenones (series C) a strong dependence occurs which demands an increasing order in the sequence **11** and **10**. This is in contrast to the behavior of the series A. One could suppose a connection with the different A/B ring junction. But for further proof of this conjecture one needs new and more experimental information. Further work is in progress.

From the data given in Table II one can estimate mean values for the tensor coordinates of the different enones (Table III). For the series A and B, as well as for the compound **2**—with the exception of the sign—the rotational strengths (R_{iso}^{NK}) of the isotropic state are nearly equal. For **2** Djerassi and co-workers[15] assumed from ORD measurements that the chromophore is in an equal but antipodal form compared to the skeleton of **1**. With the knowledge of the different tensor coordinates (Table III) we can again raise the question whether one can conclude that the same value of R_{iso}^{NK} for two compounds and an equal or similar band structure of the CD and ORD curve are an unequivocal proof for the fact that the chromophore has the same or antipodal geometrical structure. If this were true, the different tensor coordinates, e.g., of the series A, B and C, should be a consequence of the different orientation of the chromophore with respect to the direction of propagation of light. This can occur if the parts of the molecule which are responsible for the orientation (skeleton) are bound in a distinct way to the chromophore. In order to prove this assumption one has to look for a method to compare the different types of molecules. The chromophore of the series B can be transformed to that of the series A by rotating the chromophore by 180° about the x_3 axis. This rotation has no influence on the tensor coordinates and therefore $\Delta\epsilon^A(\bar{\nu})$ and $R_{11}^{NK} + R_{22}^{NK}$ and R_{33}^{NK} should be the same, i.e., the tensor is invariant to this rotation. This is in contradiction to the experimental behavior. The chromophore in the A and B series, therefore, must have a different structure. In an equivalent way the compound **2**[22] can be compared[4] with the series A and B. In contradiction to the premise two different sets of tensor coordinates $R_{11}^{NK} + R_{22}^{NK}$ and R_{33}^{NK} can be evaluated. It is not known, if at all, which set is correct. Therefore we have to conclude that an equal rotational strength $R_{\mathrm{iso}}^{\mathrm{NK}}$ and an equal or similar band structure can but must not be a consequence of the same geometrical structure of the chromophore. From this point of view a separation of the sum $R_{11} + R_{22}$ by comparing the tensor coordinates of two compounds, as we have done earlier,[4] seems not to be realistic.

The coordinates of the tensor of rotation for a transition K ← N are given by

$$R_{11}^{\mathrm{NK}} = -\langle\mu_2\rangle_{\mathrm{NK}}\left\{\frac{i}{2}\langle m_2\rangle_{\mathrm{KN}} + \frac{\omega_{\mathrm{KN}}}{4c}\langle Q_{31}\rangle_{\mathrm{KN}}\right\} - \langle\mu_3\rangle_{\mathrm{NK}}\left\{\frac{i}{2}\langle m_3\rangle_{\mathrm{KN}} - \frac{\omega_{\mathrm{KN}}}{4c}\langle Q_{21}\rangle_{\mathrm{KN}}\right\} \tag{7a}$$

$$R_{22}^{\mathrm{NK}} = -\langle\mu_1\rangle_{\mathrm{NK}}\left\{\frac{i}{2}\langle m_1\rangle_{\mathrm{KN}} - \frac{\omega_{\mathrm{KN}}}{4c}\langle Q_{32}\rangle_{\mathrm{KN}}\right\} - \langle\mu_3\rangle_{\mathrm{NK}}\left\{\frac{i}{2}\langle m_3\rangle_{\mathrm{KN}} + \frac{\omega_{\mathrm{KN}}}{4c}\langle Q_{12}\rangle_{\mathrm{KN}}\right\} \tag{7b}$$

$$R_{33}^{\mathrm{NK}} = -\langle\mu_1\rangle_{\mathrm{NK}}\left\{\frac{i}{2}\langle m_1\rangle_{\mathrm{KN}} + \frac{\omega_{\mathrm{KN}}}{4c}\langle Q_{23}\rangle_{\mathrm{KN}}\right\} - \langle\mu_2\rangle_{\mathrm{NK}}\left\{\frac{i}{2}\langle m_2\rangle_{\mathrm{KN}} - \frac{\omega_{\mathrm{KN}}}{4c}\langle Q_{13}\rangle_{\mathrm{KN}}\right\} \tag{7c}$$

$\langle\mu_i\rangle_{\mathrm{NK}}$ and $\langle m_i\rangle_{\mathrm{KN}}$ ($i = 1, 2, 3$) are the electric and magnetic dipole transition moment, respectively; $\langle Q_{ij}\rangle_{\mathrm{KN}}$[24] ($i,j = 1, 2, 3$) is the electric quadrupole transition moment; $\omega_{\mathrm{KN}} = (E_{\mathrm{K}} - E_{\mathrm{N}})/\hbar$; E_{K} and E_{N} are the energies of the states K and N; $c \equiv$ velocity of light in vacuo.

Because of the special definition of the molecule fixed coordinate system ($\langle\mu_1\rangle_{\mathrm{NK}} = 0$) the tensor coordinates R_{22}^{NK} and R_{33}^{NK} can be simplified to

$$R_{22}^{\mathrm{NK}} = -\langle\mu_3\rangle_{\mathrm{NK}}\left\{\frac{i}{2}\langle m_3\rangle_{\mathrm{KN}} + \frac{\omega_{\mathrm{KN}}}{4c}\langle Q_{12}\rangle_{\mathrm{KN}}\right\} \tag{8a}$$

$$R_{33}^{\mathrm{NK}} = -\langle\mu_2\rangle_{\mathrm{NK}}\left\{\frac{i}{2}\langle m_2\rangle_{\mathrm{KN}} - \frac{\omega_{\mathrm{KN}}}{4c}\langle Q_{13}\rangle_{\mathrm{KN}}\right\} \tag{8b}$$

With the sole knowledge of $R_{11}^{\mathrm{NK}} + R_{22}^{\mathrm{NK}}$ and R_{33}^{NK} there is no possibility for a quantitative calculation of the quadrupole contribution. From the dipole strength and the direction of the transition moment the absolute values of $|\langle\mu_2\rangle_{\mathrm{NK}}|$ and $|\langle\mu_3\rangle_{\mathrm{NK}}|$ can be evaluated. For the series A, e.g., with a mean value $\bar{D} = 6.17 \times 10^{-38}$ cgs and a direction of the transition moment of about −58° with respect to the x_2 axis[5] (see Figure 1) the two values are $|\langle\mu_2\rangle_{\mathrm{NK}}| = 1.3 \times 10^{-19}$ cgs (0.13 D), $|\langle\mu_3\rangle_{\mathrm{NK}}| = 2.1 \times 10^{-19}$ cgs (0.21 D). Furthermore, from R_{33}^{NK} (eq 8b) and $|\langle\mu_2\rangle_{\mathrm{NK}}|$ the sum $-i\langle m_2\rangle_{\mathrm{KN}} + (\omega_{\mathrm{KN}}/2c)\cdot\langle Q_{13}\rangle_{\mathrm{KN}} \approx 6 \times 10^{-21}$ cgs can be calculated.

For the type of transition we have analyzed here, we would expect that it is mainly a n–π* transition which is an allowed magnetic dipole transition. For the series A the magnetic dipole transition moment should be parallel to the C═O bond direction and therefore nearly parallel to the x_3 direction (Figure 1). Accepting for $|\langle m_3\rangle_{\mathrm{KN}}|$ a value of + or − 1 μ_{B}, as often done, we can estimate from $R_{11}^{\mathrm{NK}} + R_{22}^{\mathrm{NK}} - R_{33}^{\mathrm{NK}}$ and $|\langle\mu_3\rangle_{\mathrm{NK}}|$ the quadrupole transition moment $|\langle Q_{13}\rangle_{\mathrm{KN}}| \approx 6 \times 10^{-26}$ or 3×10^{-25} cgs. From this $|\langle m_2\rangle_{\mathrm{KN}}|$ can be calculated to ±1–2 μ_{B}. This value seems to be large for this type of transition and can only be understood by the assumption that the chromophore is inherently dissymmetric.

These numbers given for the series A can only be seen as a first estimation. Further information is necessary to analyze data from different compounds in order to get structural information. Also good quantum mechanical calculations of the quantities determining eq 7 seem to be essential for the problem involved here.

Acknowledgment. We thank Mr. M. Reich, who has done a large part of the CD and UV measurements. Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

References and Notes

(1) Part 4 of this series: see ref 5.
(2) E.g., M. Legrand, "Stereochemistry: Fundamentals and Methods", Vol. 2, H. B. Kagan, Ed., Georg Thieme Verlag, Stuttgart, 1977, pp 32–183.
(3) $R_{\alpha\alpha}^{\mathrm{NnKk}}$ is a coordinate of the tensor of rotation $\mathbf{R}_{ij}^{\mathrm{NnKk}}$ ($i, j = 1, 2, 3$), which is given here in the system of the principal axes.
(4) H.-G. Kuball, T. Karstens, and A. Schönhofer, *Chem. Phys.*, **12,** 1 (1976).
(5) H.-G. Kuball, J. Altschuh, R. Kulbach, and A. Schönhofer, *Helv. Chim. Acta* **61,** 571, 1510 (1978).
(6) $g_{ij33} = (1/8\pi^2)\int f(\alpha, \beta, \gamma)a_{i3}a_{j3}\sin\beta\, d\alpha\, d\beta\, d\gamma$; $\sum_{i=1}^{3} g_{ii33} = 1$; α, β, and γ are the Eulerian angles as defined earlier.[4] a_{i3}, a_{j3} are elements of the transformation matrix from the space fixed to the molecule fixed coordinate system. $f(\alpha, \beta, \gamma)$ is the orientational distribution function. The connection between the order matrix S_{ij}, introduced by Saupe,[7] and the orientational distribution coefficients is given by $S_{ij} = (g_{ij33} - \delta_{ij})/2$.
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(9) (a) E. Friedel, *C. R. Acad. Sci.*, 475 (1923); (b) H. Stegemeier, J. K. Mainusch, and E. Steiger, *Chem. Phys. Lett.*, **8,** 425 (1971).
(10) Measurements with an ac electric field (50 Hz) give a similar but not identical effect because of the somewhat different field strength dependence of the CD curve.[23]
(11) T. Karstens, Dissertation, University of Würzburg, 1973.
(12) M. Acimis, Dissertation, University of Kaiserslautern, 1976.
(13) We are grateful to Professor Dr. G. Snatzke, University of Bochum, for supplying this compound.
(14) The compounds **6–10** were placed at our disposal by Dr. G. Sauer, Schering AG, Berlin, which is gratefully acknowledged.
(15) C. Djerassi, R. Riniker, and B. Riniker, *J. Am. Chem. Soc.*, **78,** 6377 (1956).
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(18) E. Sackmann and H. Möhwald, *J. Chem. Phys.*, **58,** 5407 (1973).
(19) If eq 4 were written with the model of Saupe's order matrix,[7] ρ would have to be substituted by S_{33}.
(20) E.g., (a) P. Diehl and C. L. Khetrapal, *Mol. Phys.*, **14,** 283 (1967); (b) K. G. Orrel and V. Sik, *J. Chem. Soc., Faraday Trans. 2*, 1360 (1975).
(21) In contrast to a preceding paper[4] $R_{\mathrm{iso}}^{\mathrm{NK}}$ is defined here as the trace of the tensor of rotation in order to be consistent with the usual definition of the rotational strength. In the former paper one-third of this trace was used. As a consequence eq 6a and 6b are different from that one given earlier.[4]
(22) For this calculation we have assumed that **2** is in the antipodal state with respect to the series A or B.
(23) To be published.
(24) The quadrupole operator is defined here as $\tilde{Q}_{ij} = \sum_\nu e_\nu x_{i\nu} x_{j\nu}$; $\sum_\nu$ represents the sum over all nuclei and electrons.