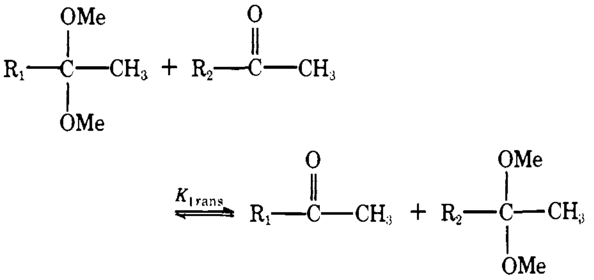
more rapidly than the entropy of the ketals. The results also indicate that branching accentuates this trend.

The exact origin of these substantial entropy differences is probably manyfold, though two important features of our system stand out. Since these effects have been characterized in a hydrogen-bonding solvent, differential solvation of the ketones and ketals could have an important contribution. Differences in electrostriction of solvent have been shown to be the key element in determining entropy effects in a variety of reactions involving polar and ionic species.[9] One way to minimize the effects of solvation would be to measure the relative free energies of hydrolysis via an acid-catalyzed transketalization reaction (eq 5). That is, knowledge of the hydrolysis equilibrium constant for either ketal in eq 5 when combined with K_{trans} would allow calculation of the other. Comparison of these values with those obtained directly in methanol solution might give a clue as to the relative magnitudes of solvation effects on the free-energy differences. Experiments of this type are currently underway.



$$\mathrm{R_1{-}C(OMe)_2{-}CH_3} + \mathrm{R_2{-}C({=}O){-}CH_3} \xrightleftharpoons{K_{\mathrm{trans}}} \mathrm{R_1{-}C({=}O){-}CH_3} + \mathrm{R_2{-}C(OMe)_2{-}CH_3} \quad (5)$$

The internal contributions to the entropy differences are most likely a function of internal rotational characteristics. A useful decomposition of these effects can be derived from empirical force field calculations, provided that a reasonable balance of internal forces is achieved.[10] We are currently engaged in attempts to generate a reliable force field for the ketones and ketals, and we shall report our results from this work at a later time.

Acknowledgment. This investigation was supported by the Office of Basic Energy Sciences, Department of Energy. We wish to thank Kurt Billet for his valuable assistance in the calorimetric studies.

References and Notes

(1) Taft, R. W. In "Steric Effects in Organic Chemistry", Newman, M., Ed.; Wiley: New York, 1956; Chapter 13.
(2) (a) Hancock, K. *J. Am. Chem. Soc.* **1961,** *83,* 4211. (b) Hanch, C.; Unger, S. H. *Prog. Phys. Org. Chem.* **1976,** *12,* 91. (c) Charton, M. *J. Org. Chem.* **1978,** *43,* 3995.
(3) Perrin, D. D. "Purification of Laboratory Chemicals", Pergamon Press: Elmsford, N.Y., 1966.
(4) Cf. Smith, E. L. *J. Chem. Soc.* **127,** 1288.
(5) Wiberg, K. B.; Squires, R. R. *J. Chem. Thermodyn.,* in press.
(6) Prosen, E. J.; Kilday, M. V. *J. Res. Natl. Bur. Stand., Sect. A* **1973,** *77,* 581.
(7) Wadsö, I.; Öjelund, G.; Hill, J. O. *J. Chem. Thermodyn.* **1969,** *1,* 111.
(8) Richie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964,** *2,* 323.
(9) (a) Hammet, L. P. "Physical Organic Chemistry", McGraw-Hill: New York, 1940; p 80 ff. (b) Taft, R. W.; Beauchamp, J. L.; Arnett, E. M. *J. Am. Chem. Soc.* **1978,** *100,* 1240.
(10) (a) Boyd, R. H. *J. Am. Chem. Soc.* **1975,** *97,* 5353. (b) Schleyer, P. v. R. *Ibid.* **1973,** *95,* 8005.

Linear and Circular Dichroism Studies of $\pi \rightarrow \pi^*$ Transitions in Steroidal Dienes and α,β-Unsaturated Ketones[1a]

Jacek Gawronski,[1b] Tommy Liljefors,[1c] and Bengt Nordén*[1d]

Contribution from Adam Mickiewicz University, Institute of Chemistry, 60-780 Poznan, Poland, and the Departments of Organic and Inorganic Chemistry 1, Chemical Center, University of Lund, P.O. Box 740, S-220 07 Lund, Sweden.
Received February 22, 1979

Abstract: The diene and α,β-unsaturated keto chromophore in different conformations and orientations in a number of steroids were studied by circular dichroism (CD) in solution and linear dichroism (LD) in a stretched polyethylene matrix. The geometries of the chromophores were obtained from force-field calculations, and the energies, transition moments, and oscillator strengths for the $\pi \rightarrow \pi^*$ transitions were calculated by the VESCF-CI method including all singly and doubly excited configurations. CD, supported by LD, confirms the presence of an additional transition around 200 nm (6 eV), not observed in the UV spectra of dienes and α,β-unsaturated ketones. An analysis of the spectra shows, in agreement with the calculations, that the first two $\pi \rightarrow \pi^*$ transitions occur close to each other in the region 200–260 nm. The importance of taking doubly excited configurations into account is demonstrated by the fact that the second transition is otherwise obtained at very high energy. The experimental and calculated transition moments were in reasonable agreement, and a rule for the transition moment direction of the first absorption band was provided by the line between the end atoms of the diene or enone moieties, even for twisted chromophores. The circular dichroism is discussed with respect to chromophore dihedral angle. Unexpectedly large rotational strengths shown by the planar conformations of the chromophore indicate a very strong influence from substituents.

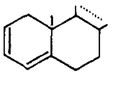
Introduction

Simple conjugated olefinic systems have been the subject of extensive theoretical and spectroscopic (UV, PE) studies over the past decade, with the aim of establishing energy levels and electronic transitions.[2] In cases where the conjugated system is part of a chiral framework, circular dichroism (CD) provides a particularly powerful method. Much attention has been paid to long-wavelength Cotton effects in dienes and α,β-unsaturated ketones,[3-5] but there has been little discussion of the short-wavelength transitions ($\pi \rightarrow \pi^*$), although they can be easily seen in the circular dichroism (CD) spectrum, as will be shown below.

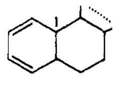
The present study is concerned with a firmer characteriza-

0002-7863/79/1501-5515$01.00/0

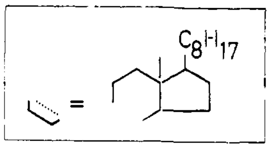
tion of the electronic properties of some basic conjugated systems. For this purpose we have used circular dichroism (CD) in combination with linear dichroism (LD) spectroscopy[6] on partially oriented solutions. Our intention is to use the information gained to reach a better understanding of the electronic states of important molecules such as steroids, carotenoids, and retinal, for which the orientations and electronic perturbations in membranes are currently being studied.[7] We have found the molecules (**1–12**) suitable for these elementary studies.

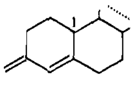


1

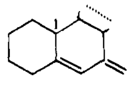


2

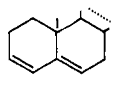




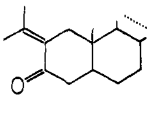
3



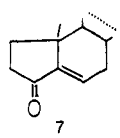
4



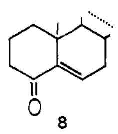
5



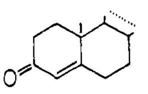
6



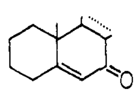
7



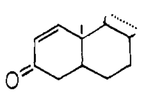
8



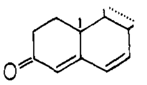
9



10



11



12

Theoretical calculations of the electronic spectra of dienes and α,β-unsaturated ketones employing all singly and doubly excited configurations in the configuration interaction consistently show two close-lying π→π* transitions in the vicinity of the observed UV absorption maximum.[8-11] Calculations using only singly excited configurations show only one transition in this spectral region. The oscillator strength of the second transition is generally calculated to be much smaller than that of the first transition. Furthermore, since the second transition in many cases is predicted to fall in an inconvenient spectral region (around 200 nm), it is not surprising that it has not been clearly observed in the UV spectrum. However, small shoulders on the short-wavelength side of the broad band and a lack of symmetry of this band indicate the presence of the second transition.[12-14]

The possibility that the two predicted π→π* transitions have Cotton effects of opposite signs makes circular dichroism spectroscopy a more promising tool for studies of the long-wavelength π→π* transitions of dienes and α,β-unsaturated ketones. Ziffer and Robinson[12] found some evidence for two transitions in the 200–250-nm region of the CD spectra of certain steroids, but were not able to give any conclusive interpretation of the nature of the new transition.

The two π→π* transitions may also differ by their transition-moment directions. This makes it of interest to investigate linear dichroism spectra in the region corresponding to the predicted absorption wavelengths. The steroid skeleton provides a long and relatively stiff structure that can be efficiently oriented when incorporated in an oriented polymer matrix. (Several of these molecules should be excellent optical probes in oriented matter, and this provides a further reason for determining the polarization of their transitions.) The present linear dichroism study is based on the partial orientation of molecules incorporated in stretched polymer films.[6] Linear dichroism of steroidal α,β-unsaturated ketones in stretched polyethylene films was first observed by Yogev et al.,[15] who noticed that molecules with the same steroid skeleton obtained equal degrees of orientation. Oriented keto steroids have later also been studied with respect to the anisotropic circular dichroism of the n→π* transitions.[16]

Methods

Linear Dichroism in Stretched Polyethylene Matrix. The reduced dichroism $\mathrm{LD}/A_{\mathrm{iso}}$ has been interpreted by employing the following formula:[6]

$$\frac{\mathrm{LD}}{A_{\mathrm{iso}}} = S_{zz}\frac{3}{2}(3\cos^2\alpha - 1) \qquad (1)$$

Since the LD method is not well-known, basic symbols are defined in the Appendix, which also contains a motivation for the special case to which eq 1 refers. Knowledge of the orientation parameter S_{zz} permits α to be estimated.

Calculations. Electronic transitions, oscillator strengths, and transition moments were calculated by the VESCF-CI method, including all singly and doubly excited configurations.[8-11] The geometries of the chromophores were calculated by a molecular mechanics method designed for conjugated systems.[9,17] The bicyclic analogues containing the conjugated system were used as models in the geometry calculations for the steroids studied (cf. Figure 8).

To enable comparison of the experimental α values with the calculated transition moment directions, an orientation axis, z, must be chosen. It was found reasonable, as a first approximation, to choose a standardized orientation axis parallel to some basic reference direction in the molecule. For example, in the keto steroid below the carbonyl bond was chosen, as it was practically parallel to the longest dimension of the calculated structures. This choice of orientation axis is essentially the same as that employed by Yogev et al.,[15] and corresponds closely to the longitudinal principal axis of inertia as calculated from X-ray data. The deviation of the true orientation axis from the standard direction can in favorable cases be discussed on the basis of a comparison of experimental and calculated α values.

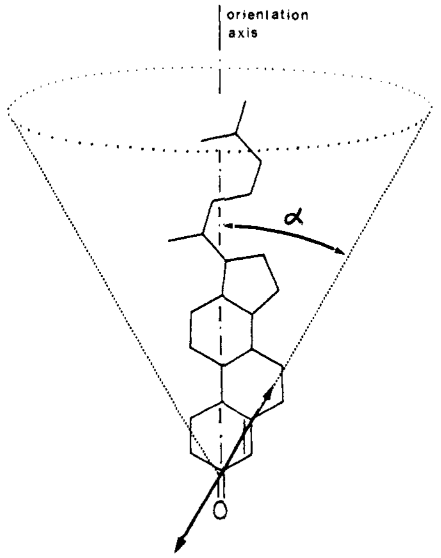


Table I. Calculated and Observed Electronic Spectra

		calcd $\pi \rightarrow \pi^*$ transitions					obsd transitions							
							UV bands[c]		CD bands[c]		LD bands[d]			
compd	no.	energy, eV	λ_{max}, nm	λ_{max}^{cor},[a] nm	oscillator strength	pol[b] α, deg	λ_{max}, nm	$\epsilon \times 10^3$, $M^{-1}\,cm^{-1}$	λ_{max}, nm	$\epsilon_l - \epsilon_r$, $M^{-1}\,cm^{-1}$	λ_{max}, nm	$(\epsilon_\parallel - \epsilon_\perp)/\epsilon$	α,[e] deg	dihedral angle ω, deg
cis dienes	**1**								194	−7.5				+11.2
		5.88	211	221	0.10	31					190–210	0.24	50 (52)	
									214	2.76				
		5.09	244	262	0.31	63	265	6.4	265	12.6	240	0.15	52 (53)	
											275	−0.04	56 (55)	
	2	6.01	206	216	0.09	32			205	−3.30	210	>0	<55	+17.4
		5.25	236	254	0.31	63	262	3.3	260	−1.87	265	−0.12	57 (56)	
trans dienes	**3**	5.98	207	212	0.16	13			196	−5.1	190–230	[f]	>30	180
		5.63	220	233	0.62	12	239	25.4	234–240	15.0	240	1.2	29 (39)	
	4	5.98	207	212	0.16	47			201	−6.9	<205	<0	>55	180
		5.63	220	233	0.62	48	240	23.8	238	−27.9	233	0.11	52 (53)	
	5	5.99	207	217	0.24	51			<190	>0				+175
							228	20.4			228	0.26		
		5.58	222	240	0.53	47	235	22.4	234.5	−14.5	237	0.34	48 (50)	
							244	14.1			245	0.36		
cis enones	**6**	6.15	202	214	0.03	58			193	−7.5	207	+0.1	53 (55)	+13
									211	0.37				
		5.42	229	242	0.36	64	246	8.0	240	−2.23	247	−0.29	61 (59)	
							323	0.055						
	7	6.31	197	209	0.01	67			<190	<0	<200	<0	>55	+13
									216	−6.0				
		5.74	216	240	0.42	9	238	10.0	255	0.77	235	0.19	51 (52)	
							346	0.031	344	−1.45				
	8	6.57	189	201	0.06	54								+32
		5.73	216	240	0.29	16	234	7.15	226	−7.0	237	1.48	35 (36)	
									260	+0.1	260	[f]		
									334	1.08	330	>0		
trans enones	**9**	6.34	196	208	0.05	35			208	11.8	190–210	[f]	>42	180
		6.00	207	229	0.68	13	232	16.6	230	7.3	235	0.63	42 (46)	
							337	0.044	337	−1.6				
	10	6.34	196	208	0.05	23			205	−21.0	<205	[f]	>45	180
		6.00	207	229	0.68	45	230	14.6	228^{s}	−14.5	232	0.45	45 (49)	
									337	1.49				
	11	6.49	191	203	0.08	28			200	−10.2	<205	[f]	>20	+179
		6.21	200	222	0.66	12	223	9.6	226.5	11.6	227	1.61	18 (34)	
							344	0.028	349	−0.94				
dienone	**12**	6.21	200	217	0.02	34			217	−2.42				+179, +174
									224	−3.40	200–230	[f]	(>30)	
		5.46	227	244	0.03	42			230	−3.25				
		5.27	235	266	1.04	18	272	29	274	−3.0	275	1.89	0 (30)	
							355	0.063	370	3.0				

[a] Corrected for solvent by −0.30 eV for enones and by +8 nm for dienes, also including corrections due to ring closure of enones (+12 nm) and to "cis-alkyl effect" in dienes (+5 nm). [b] Calculated using the polarization axes shown in Figure 8. [c] In *n*-heptane. [d] In oriented polyethylene matrix. [e] From eq 1 for $S = 0.63$ (corresponding to $\alpha = 0$ for compound **12**); limiting value corresponding to $S = 1$ given in parentheses. [f] Decrease in $(\epsilon_\parallel - \epsilon_\perp)/\epsilon$.

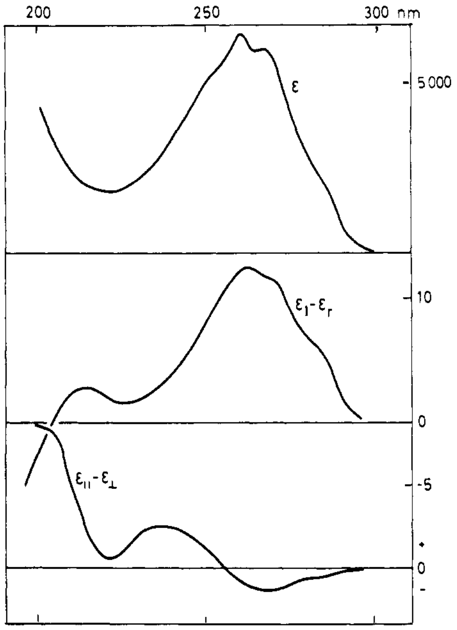


Figure 1. Absorption, circular dichroism, and linear dichroism spectra of cholesta-2,4-diene (compound **1**). The extinction coefficient ϵ (M^{-1} cm^{-1}) and the circular dichroism $\epsilon_l - \epsilon_r$ (M^{-1} cm^{-1}) refer to n-hexane solvent. The linear dichroism $\epsilon_\| - \epsilon_\perp$ (arbitary units) refers to stretched polyethylene matrix ($\|$ = stretch direction); cf. Table I.

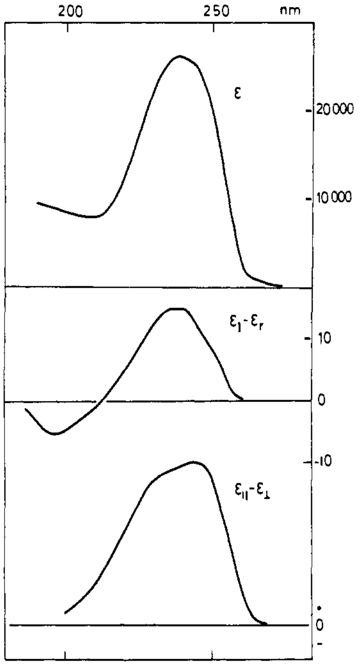


Figure 2. Absorption, circular dichroism, and linear dichroism spectra of 3-methylenecholest-4-ene (compound **3**). Otherwise as in Figure 1.

Experimental Section

Absorbance and circular dichroism spectra were recorded in n-heptane solutions on a Cary 118-C and a Jobin-Yvon Dichrographe III. Linear dichroism (LD) spectra were measured on a Jasco J-40 spectropolarimeter converted to LD by means of a quarter-wave prism.[18] A_{iso} was obtained as described in the Appendix. The solutes were transferred to stretched polyethylene strips (20 × 20 × 0.05 mm stretched 500%) by allowing the strip to be in contact with a concentrated chloroform solution for several hours. The steroids were prepared and purified according to standard methods.

Results

The observed and calculated energies, absorption intensities, and polarizations of the $\pi \rightarrow \pi^*$ transitions of the molecules examined are given in Table I, together with the observed circular dichroisms in the UV region. The UV, CD, and LD spectra of some of the molecules are shown in Figures 1-7.

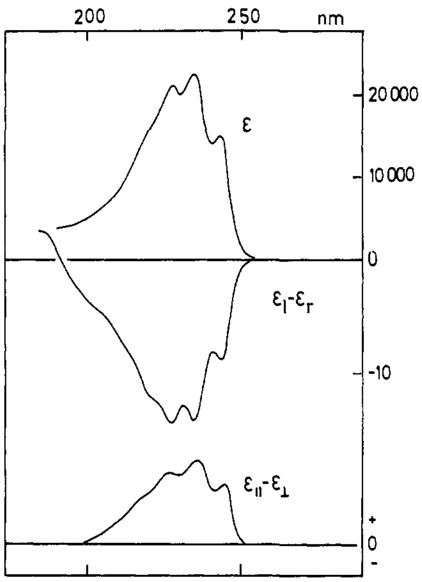


Figure 3. Trans diene **5**. Otherwise as in Figure 1.

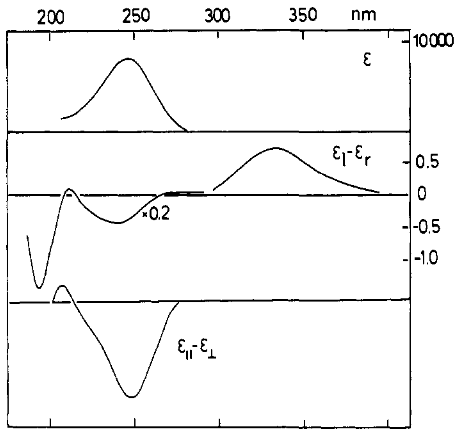


Figure 4. Cis enone **6**. Otherwise as in Figure 1.

UV Spectra. The UV spectra of all the chromophores studied show only one strong band in the short-wavelength region (190-260 nm), and thus give evidence for the presence of only one transition in this energy region (the shape of the UV band of compound **5** is due to vibrational fine structure of one transition). The spectra in polyethylene were found to be practically identical with those in n-heptane (cf. Figure 6), and therefore only the latter are usually displayed.

CD Spectra. The circular dichroism of almost all compounds studied here confirms the presence of an additional transition around 200 nm not previously observed in the UV spectra of dienes and α,β-unsaturated ketones. It is seen in compound **1** at 214 nm, **2** at 205 nm, **3** at 196 nm, **4** at 201 nm, **6** at 190-210 nm, **9** at 208 nm, **10** at 205 nm, and **11** at 200 nm. In **5**, **7**, and **8** only an indication of a second transition (below 190 nm) is obtained. In **7** and **8** small positive CD peaks are observed in the long-wavelength tails of the main absorption bands. This can indicate two close-lying electronic transitions, but it cannot be excluded that the effect is due to two vibronic components of the same transition (with opposite rotational strengths). In all ketones the well-characterized $n \rightarrow \pi^*$ carbonyl transition dominates the long-wavelength UV circular dichroism.

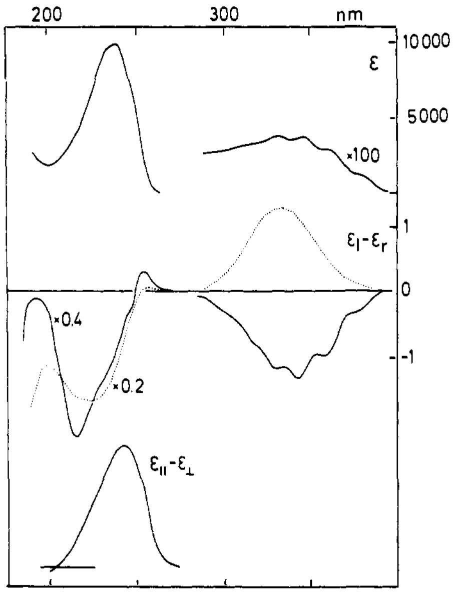


Figure 5. Cis enone **7**. Otherwise as in Figure 1. (Cis enone **8** dotted CD curve.)

In order to compare the effects of solvent interactions on the two $\pi \rightarrow \pi^*$ transitions the CD spectrum was measured in methanol on compound **11**, which provides the best resolved CD peak of the second transition. The peaks were shifted from 200 and 226.5 (*n*-heptane) to 204 and 236 nm (methanol). Taking the effects on the apparent CD maxima due to overlapping into account, the conclusion is a strong shift of the lowest transition and no significant shift of the second transition.

LD Spectra. The main information provided by the linear dichroism spectra is the polarization of the first transition. Owing to the limited transparency of the matrix it was generally not possible to clearly resolve the second transition. However, the presence of a second absorption component with different polarization could be observed in many of the compounds as a strong change in the ratio $(\epsilon_\parallel - \epsilon_\perp)/\epsilon$ or even by a sign change.

The definition of the orientation parameter S_{zz} in eq 1 is given in the Appendix. The largest LD/$A_{\rm iso}$ was observed for dienone **12** and provides a lower limit of $S_{zz} = 0.63$. This value and the upper limit (1.00) were used to obtain the experimental α values presented in Table I.

Calculations. The calculated transition energies, absorption maxima, and oscillator strengths are given in Table I. To make a comparison with experimental data possible, the calculated transition wavelengths must be corrected for solvent effects and for certain other effects not taken into account by the calculations. The longest wavelength $\pi \rightarrow \pi^*$ transitions of the enones have been corrected for solvent by subtracting 0.30 eV (10-13 nm). This is the mean difference between absorption maxima in the vapor phase and in hexane solution for a number of α,β-unsaturated aldehydes and ketones.[19,20] (The difference between hexane and heptane solution should be insignificant.) The corresponding absorption maxima for dienes were corrected by +8 nm.[10] While the necessary solvent correction for the longest wavelength $\pi \rightarrow \pi^*$ transition is easily evaluated from experiments, this is not so for the second transition. The position of the absorption maximum in UV is dominated by the first strong transition. Preliminary studies, described above, indicated that the second transition has a much smaller solvent effect than the first one. For this reason we have not corrected the second $\pi \rightarrow \pi^*$ transition for a solvent effect in this paper.

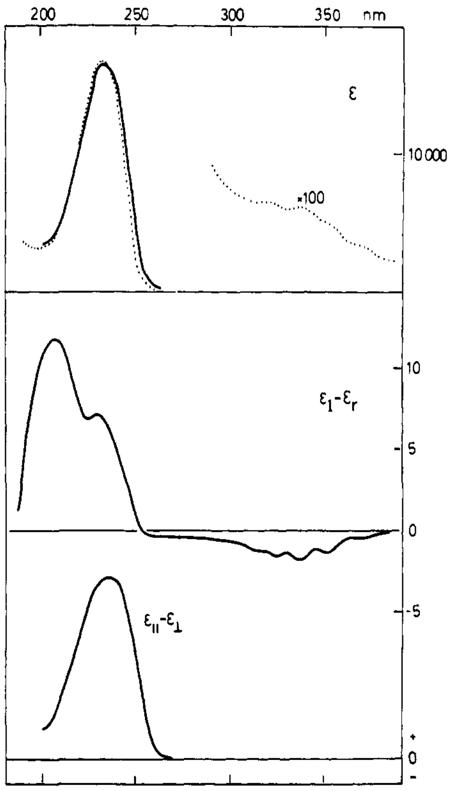


Figure 6. Trans enone **9**. Otherwise as in Figure 1. In the absorption spectrum the full and the dotted curves refer to polyethylene and *n*-heptane solvents, respectively.

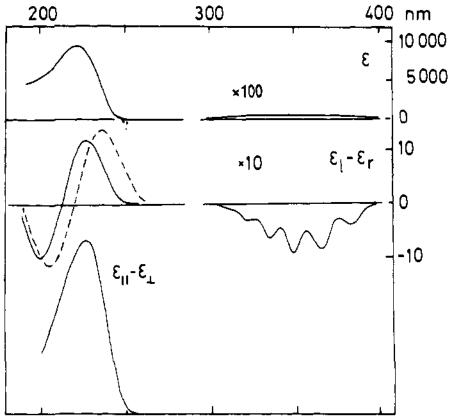


Figure 7. Trans enone **11**. In circular dichroism the solvent shift in methanol (dashed curve) is shown. Otherwise as in Figure 1.

Two other corrections to the calculated absorption wavelengths must be made. For cyclic enones a "ring-closure" correction is necessary, as discussed in detail by Liljefors and Allinger.[11] Similarly, the "cis-alkyl" effect in dienes must be taken into account.[10] These corrections are included in $\lambda_{\max}^{\rm cor}$ in Table I.

For all enones and dienes investigated (**1-11**), two $\pi \rightarrow \pi^*$ transitions are predicted above 200 nm ($\lambda_{\max}^{\rm cor}$), and the longest wavelength transition is predicted to have the largest oscillator strength. The calculated absorption wavelengths are, for both transitions, in satisfactory agreement with the experimental values. The lowest energy $\pi \rightarrow \pi^*$ state is strongly dominated by the singly excited configuration in which one electron is promoted from the highest occupied orbital to the lowest unoccupied one. The second close-lying $\pi \rightarrow \pi^*$ state is a mixture of singly and doubly excited configurations. The most important doubly excited configuration is that in which the two electrons in the highest occupied orbital are placed in

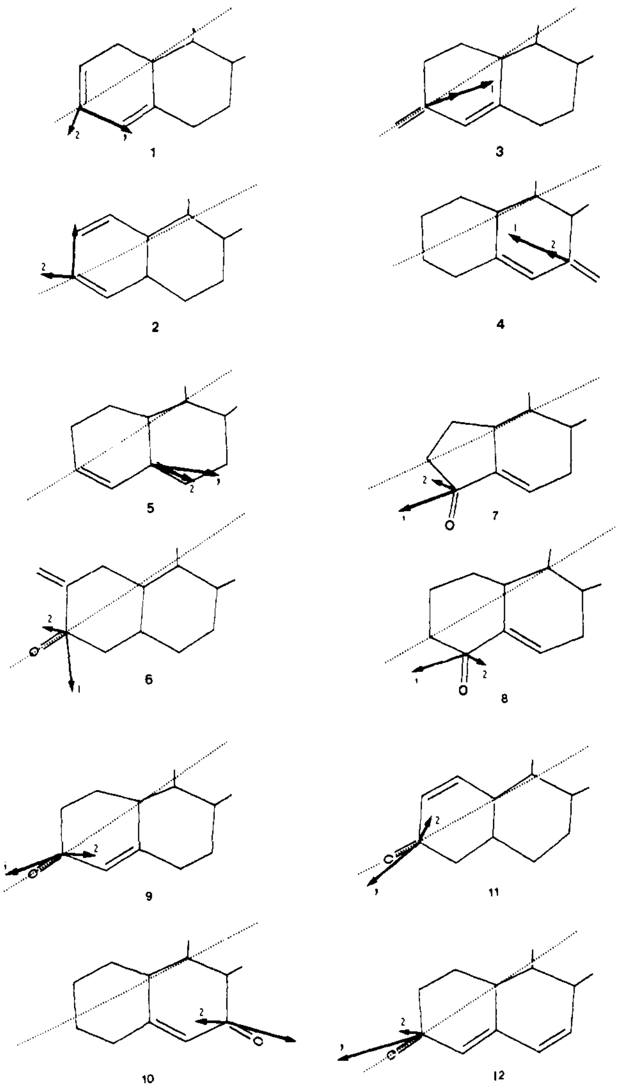


Figure 8. Calculated transition moment vectors (twice the calculated length, per unit charge) for the two $\pi \rightarrow \pi^*$ transitions above 200 nm (the longest wavelengths are denoted 1). The geometries of the compounds are shown as calculated by molecular mechanics. The projection plane is defined by the carbon atom constituting the origin of the transition moment vectors and the two adjacent chromophore atoms, except in 7 and 8, where the C—C=C fragment defines the plane. The dotted lines represent the assumed directions of the orientation axes.

the lowest unoccupied one. The effect of including doubly excited states has previously been discussed in detail.[2,9,10]

The separation between the two $\pi \rightarrow \pi^*$ transitions above 200 nm is significantly larger for s-cis than for s-trans compounds. This is a consequence of differences in twist around the central single bond of the chromophore. All s-cis compounds are significantly more twisted around this bond than are the s-trans compounds (see Table I). The separation of the two transitions increases rapidly as the dihedral angle of the chromophore deviates from 0 and 180°.[11]

The calculated transition moments are shown in Figure 8. For comparison with experimental polarization angles obtained from LD spectra, the angle between the assumed orientation axes, as described above and shown in Figure 8, and the transition moments were calculated. The angles are given as $0° \leq \alpha \leq 90°$ for the purpose of comparison with experiment, and are included in Table I.

Discussion

Transition Moments and Geometry. With a few exceptions there is agreement between experimental and calculated transition moment directions α. To illustrate the possibilities of LD spectroscopy in this study, let us discuss a few molecules in some detail.

The cis diene **1** shows two LD bands of opposite signs at the position of the first absorption band (Figure 1). $\mathrm{LD}/A_{\mathrm{iso}}$ is small for both, indicating that α is close to the point (54.7°) where the LD changes sign. The LD spectrum can then be expected to be particularly sensitive to perturbation of the polarization and the presence of the two LD bands can be explained by vibrational perturbations of a single electronic transition, resulting in slightly different polarizations in the high- and low-energy parts of the absorption band. The oscillator strength is not very large, and a vibrational structure is in fact seen in the absorption. The second transition also appears to have a weak $\mathrm{LD}/A_{\mathrm{iso}}$, but it is clearly positive, indicating that $\alpha < 55°$. The diene **2** shows a similar picture with both transitions polarized not far from 55°. For both compounds the observed behavior is in qualitative agreement with the predicted α values. Even better agreement may be obtained if the orientation axis is slightly turned (see Figure 8), like the orientation axis drawn in the illustration given in the Methods section. This illustration also demonstrates the ambiguity due to the behavior of the transition moments as "nonpolar" vectors and the equivalence of all transitions on a cone with the angle α around the orientation axis. This explains why the two transitions in **1** and **2** can have almost the same α, although their transition moments are perpendicular to each other.

In the trans dienes, the α values predicted for the first transition are in acceptable agreement with the observed polarizations. However, the second transition, which is calculated to be parallel to the first one, is found to have a significantly lower $\mathrm{LD}/A_{\mathrm{iso}}$ in **3** and **4**, indicating a larger α. However, the oscillator strength is fairly weak and it cannot be excluded that the effective polarization is slightly modified by vibronic perturbation or that there is a certain overlap from higher transitions. The fact that the second transition comes out parallel to the first can also be due to the overestimation of the influence of the first excited state. (The calculated energy separation between the first two transitions in both **3** and **4** is only 0.35 eV.)

Among the cis enones, the LD results for **6** and **8** are well accounted for by the predicted α values. The calculated α values for the transitions in **6**, close to and on each side of the angle at which the sign changes, are a sensitive indication that the orientation axis is appropriately chosen. The large $\mathrm{LD}/A_{\mathrm{iso}}$ at 237 nm in **8**, indicating a small α, is in agreement with the assignment of the first transition to this position; the second transition, as expected from the calculations, is accessible neither in the LD nor in the CD spectrum. Compound **7** is predicted to behave in a similar way, with a high $\mathrm{LD}/A_{\mathrm{iso}}$ for the first transition. However, here we have a surprising departure from the general agreement between predicted and observed polarizations. If the theoretical transition moment is correct, the low $\mathrm{LD}/A_{\mathrm{iso}}$ must be due either to an S_{zz} about ten times lower than for the other compounds or to an error of ca. 40° in the assumed orientation direction. In fact, it is possible that the different geometry of **7**, with a five-membered instead of a six-membered ring, can provide a changed S_{zz} as well as a markedly different preferred orientation direction.

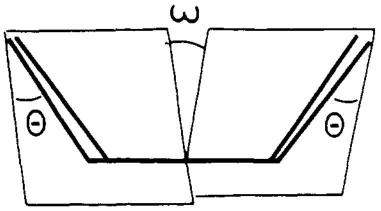
The experimental polarizations of the first transitions in the trans enones **10** and **11** are in excellent agreement with the predicted α values. The experimental results for the second transitions are fairly uncertain and do not justify any detailed conclusions. The LD is still positive, but a decreased $\mathrm{LD}/A_{\mathrm{iso}}$ may indicate an α larger than for the first transition. The dienone **12** exhibits the largest $\mathrm{LD}/A_{\mathrm{iso}}$, which was also the reason for its inclusion in the present series (cf. Appendix). The predicted $\alpha = 18°$ is in agreement with the limits $0° < \alpha < 30°$ corresponding to $0.63 < S < 1$. A lower but still positive

LD/A_{iso} observed at shorter wavelength is also consistent with the calculated $\alpha = 42$ and 34° for the following transitions.

Finally, the effect of doubly excited configurations on the calculated polarizations will be briefly discussed (Table I shows the α values obtained with all singly and doubly excited configurations). For the cis dienes the results with and without consideration of doubly excited states were practically identical, and for the trans dienes the inclusion of doubly excited configurations only implied some changes in lengths of the transition-moment vectors. For the second transition of the cis enones, the more extensive CI causes a decreased transition moment, by a factor of 2 or 3, but no important changes in direction. A considerable difference was, however, noticed for the trans enones, for which the inclusion of doubly excited configurations rotated the transition moments nearly exactly 90° and changed the α values from ca. 60° (singly excited configurations) to ca. 30° (singly and doubly excited configurations).

Circular Dichroism and Conformation. Studies of chiral dienes have allowed the formulation of the rule that cisoid dienes twisted in the sense of a right-handed helix exhibit a strong positive Cotton effect for the long-wavelength absorption band.[21] This rule has been extended to α,β-unsaturated ketones and to transoid diene conformations,[22] and more recently it has been confirmed from SCF-CNDO-CI calculations on butadiene and acrolein.[23] The predicted variation of the rotational strength with the dihedral angle ω agrees with the equation[24]

$$R_B = R^0 \cos^2 \theta \sin \omega \qquad (2)$$



where the constant R^0 is positive, $0° < \theta < 90°$, $-180° < \omega < 180°$, and the sign of ω is defined as indicated below. With θ fixed (ca. 30°), R_B is a maximum for $\omega = 90°$ and zero at 0 and ±180°. Inspection of Table I, where the calculated dihedral angles have been included, shows no immediate agreement with the CD of the first $\pi \rightarrow \pi^*$ band. The strongest circular dichroisms are actually found when ω is 180° or close to 180° (the trans dienes **3-5** and the trans enones **9** and **10**), i.e., when the chromophore is no longer dissymmetric. For a near-planar chromophore, the second factor of the rotational strength, the magnetic transition moment, of any $\pi \rightarrow \pi^*$ transition, is nearly orthogonal to the electric transition moment and the rotational strength is approximately zero:

$$R = -i \, \langle \pi | \boldsymbol{\mu} | \pi^* \rangle \cdot \langle \pi^* | \mathbf{m} | \pi \rangle \qquad (3)$$

However, the electric transition moment is large, particularly for the trans dienes, and any conceivable parallel component $\langle \pi^{*\prime} | \mathbf{m} | \pi' \rangle$ due to perturbation from the substituents (the chiral steroid framework) will therefore result in a CD of corresponding magnitude. Without knowledge of the nature of the perturbed states π' and $\pi^{*\prime}$, we cannot predict even the sign of this CD.

Several authors[5,25,26] have observed that the sign and magnitude of the lowest Cotton effect in dienes show a marked dependence on substitution, and it has been stressed that these effects are not necessarily related to conformational changes.[25] The present observation of strong CD in planar chromophores supports the conclusion of an important electronic influence from the substituents. Before CD can be used for drawing conclusions about conformation it seems therefore necessary to perform a detailed study of the substituent effects, preferably on simple rigid model chromophores.

Table II. Singlet Transition in Butadiene[a]

mode	trans diene[b]	cis diene[c]	nonplanar[d]
B	$1^1A_g \rightarrow 1^1B_u$ $\mu_{x,y} \neq 0, m = 0$	$1^1A_1 \rightarrow 1^1B_2$ $\mu_x \neq 0, m_y = 0$	$1^1A \rightarrow 1^1B$ $\mu_{x,y} \neq 0, m_{x,y} = 0$
A	$1^1A_g \rightarrow 2^1A_g$ $\mu = 0, m_z \neq 0$	$1^1A_1 \rightarrow 2^1A_1$ $\mu_z = 0, m = 0$	$1^1A \rightarrow 2^1B$ $\mu_z \neq 0, m_z \neq 0$

[a] μ and m denote the electric and magnetic transition dipole moments. [b] C_{2h}, z is the C_2 axis. [c] C_{2v}, z is the C_2 axis, x is the single bond. [d] C_2 symmetry, z is the C_2 axis.

Comparison with Butadiene and Acrolein. The relative intensities of absorption and circular dichroism may be discussed in terms of the selection rules for the butadiene and acrolein chromophores, for those of the present diene and enone systems which are nearly planar. In the butadiene π-electron system two states A and B give rise to the lowest singlet transitions. These transitions are characterized in Table II. Overlap by the electric dipole allowed $^1A_g \rightarrow {}^1B_u$ transition in trans dienes has prevented the identification of the forbidden $^1A_g \rightarrow {}^1A_g$ transition from the UV spectrum (see, e.g., **3**, Figure 2). However, the magnetic dipole allowedness provides a comparatively large rotational strength so that it can be easily observed in the CD spectrum (196 nm in Figure 2). In the case of the isoelectronic acrolein π system, contributions from carbonyl transitions at higher energies may occur, but one may still consider the strong UV band as derived from the $^1A_g \rightarrow {}^1B_u$ transition in butadiene. The second transition, with weak absorption intensity and strong CD, may be assigned to a $^1A_g \rightarrow {}^1A_g$ kind of transition. Configuration interaction can of course make this last identification questionable.

Conclusions

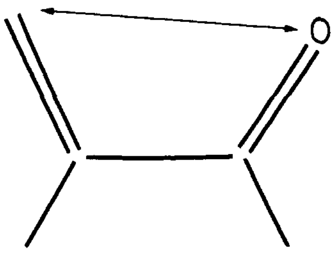
1. Circular dichroism, supported by linear dichroism, clearly shows the presence of a second $\pi \rightarrow \pi^*$ transition in dienes and α,β-unsaturated ketones, which occurs around 6 eV.

2. Calculations employing all singly and doubly excited configurations predict the first two $\pi \rightarrow \pi^*$ transitions to occur close to each other in the region 200-260 nm, for all of the conformations of these chromophores considered in this work. The importance of taking extensive configuration interaction into account, at least including doubly excited configurations, is demonstrated by the fact that the second $\pi \rightarrow \pi^*$ state would otherwise have been obtained at an unreasonably high energy, which explains why early calculations cannot have stimulated any search for this transition.

3. General agreement between calculated and observed polarizations of the first $\pi \rightarrow \pi^*$ transition and the conceptual simplicity of linear dichroism spectroscopy make us suggest that LD can be valuable for conformational analysis. This possible application will be examined for suitable systems.

The present results indicate a correlation between geometry and polarization which can be formulated in terms of a simple rule of thumb for the transition moment direction of the first absorption band of enones and dienes: *the transition moment is parallel to a line between the end atoms of the chromophore.* We have found that the rule is also correct within 5-10° for the three-dimensional conformations. For example, see structure I. The rule is also valid for the dienone **12.** However, the complicated and varying nature of the second absorption band as a consequence of configuration interaction prevents such a generalization for this case.

4. Unexpectedly large rotational strengths shown by the planar conformation of the present chromophores show that the nodal properties of the wave functions are strongly perturbed by the substituents. This indicates that circular di-



I

chroism as a simple index of conformation may be questioned in this type of system.

Appendix

Transition Moment Directions from LD. Linear dichroism, $\mathrm{LD} = A_\parallel - A_\perp$, of a sample is the differential absorbance of linearly polarized light due to different molecular extinction coefficients $\epsilon_\parallel$ and $\epsilon_\perp$ when the electric vector of light is parallel to the respective laboratory-fixed coordinate axes Z and Y:

$$\mathrm{LD} = Cl(\epsilon_\parallel - \epsilon_\perp) \qquad \text{(A1)}$$

In this expression C is the concentration of the absorbing molecule and l the path length through the sample. The factor Cl is eliminated in the "reduced dichroism" $\mathrm{LD}/A_{\mathrm{iso}}$ where $A_{\mathrm{iso}} = Cl(\epsilon_Z + \epsilon_Y + \epsilon_X)$ is the absorbance of the corresponding isotropic sample. If the orientational distribution is uniaxial with respect to Z, A_{iso} can be obtained by measuring the ordinary unpolarized absorbance, A, with X as the direction of propagation (eq 10 in ref 6).

$$A_{\mathrm{iso}} = A - \mathrm{LD}/6 - \log[2(2 + 10^{-\mathrm{LD}} + 10^{\mathrm{LD}})^{-1/2}] \qquad \text{(A2)}$$

The last term of the right-hand side of this equation may usually be omitted. The linear dichroism of the uniaxial sample is related to the orientation parameters S_{ii} and S_{ij}:

$$\epsilon_\parallel - \epsilon_\perp = \epsilon_z S_{zz} + \epsilon_y S_{yy} + \epsilon_x S_{xx} + S_{ij} \text{ cross terms} \qquad \text{(A3a)}$$

$$S_{ii} = {}^1\!/_2(3\ \langle \cos^2 Zi \rangle - 1) \qquad \text{(A3b)}$$

$$S_{ij} = {}^1\!/_2(3\ \langle \cos Zi \cos Zj \rangle)\, i \neq j \qquad \text{(A3c)}$$

In these equations $i = x, y,$ and z are molecule-fixed axes, the ϵ_i are extinction coefficients along these axes, and Zi denotes the angle between the molecule axis i and the unique sample axis Z. $\langle\ \rangle$ denotes an average taken over all molecules. The molecule axes can theoretically always be chosen so that the S_{ij} cross terms vanish. For a planar molecule $S_{xj} = 0$ if x is taken perpendicular to the plane. If the z axis (in plane) is chosen to maximize S_{zz}, the other cross terms vanish as well. The orientation of a molecule in a polymer matrix is determined by repulsion and dispersion forces, and the z axis can usually be chosen with sufficient accuracy by inspection of the molecular geometry. The steroid skeleton provides an "effective plane" and the natural choice of axis is z (orientation axis) = the long axis, y = the axis in the plane. Then from eq A1–A3 we get

$$\frac{\mathrm{LD}}{A_{\mathrm{iso}}} = \frac{\epsilon_z S_{zz} + \epsilon_y S_{yy} + \epsilon_x S_{xx}}{\epsilon_z + \epsilon_y + \epsilon_x}$$

$$S_{xx} \leqslant S_{yy} \leqslant S_{zz} \qquad \text{(A4)}$$

Since $S_{xx} + S_{yy} + S_{zz} = 0$, there are only two independent orientation parameters. They can usually be determined fairly accurately in symmetric molecules where one or several of the components ϵ_i can be concluded to be zero. However, in the present molecules a transition moment can have any direction, and all three ϵ_i can therefore be nonzero at the same time.

In the present study we shall put $S_{xx} = S_{yy}$. This assumption can be justified as follows. Obviously, $0 \leqslant S_{yy} - S_{xx} = 2S_{yy} + S_{zz} \leqslant 1 - S_{zz}$ so the larger S_{zz} the smaller is the difference. ($S_{zz} = 1$ corresponds to complete orientation.) If, e.g., $S_{zz} \geqslant 0.7$, $-0.35 \leqslant S_{yy} \leqslant -0.20$ and $-0.5 \leqslant S_{xx} \leqslant -0.35$. One can in fact from studies of the orientation of molecules with different dimensions (in the same polyethylene matrix) infer that the difference $S_{yy} - S_{xx}$ must be still smaller: from the behavior of similarly shaped molecules[27] the steroids can be expected to have S_{zz} around 0.5–0.7 and $S_{yy} - S_{xx}$ less than 0.05, i.e., $S_{yy} \approx S_{xx}$ around -0.25 to -0.35.

When $S_{yy} = S_{xx}$ ($= -S_{zz}/2$) eq A4 is conveniently written

$$\mathrm{LD}/A_{\mathrm{iso}} = S_{zz}\,\frac{3}{2}\,(3\cos^2\alpha - 1) \qquad \text{(A5)}$$

where α is the angle between the transition moment and the orientation axis z.

References and Notes

(1) (a) This work was supported by the Swedish Natural Science Research Council (Contract K 3216-008). (b) Adam Mickiewicz University. (c) Department of Organic Chemistry, University of Lund. (d) Department of Inorganic Chemistry, University of Lund.

(2) B. S. Hudson and B. E. Kohler, *Annu. Rev. Phys. Chem.*, **25**, 437 (1974).

(3) L. Velluz, M. Legrand, and R. Viennet, *C. R. Acad. Sci.*, **261**, 1687 (1965).

(4) Kam-Khow Cheong, A. Oshita, D. J. Caldwell, and H. Eyring, *Top. Mod. Phys.*, 93 (1971).

(5) A. W. Burgstahler, R. C. Barkhurst, and J. Gawronski in "Modern Methods of Steroid Analysis", E. Heftmann, Ed., Academic Press, New York, 1973, Chapter 16; J. Gawronski, *Tetrahedron*, **33**, 1235 (1977).

(6) For a review of this technique see B. Nordén, *Appl. Spectrosc. Rev.*, **14**, 157 (1978).

(7) B. Nordén, G. Lindblom, and I. Jonas, *J. Phys. Chem.*, **81**, 2086 (1977).

(8) N. L. Allinger, T. W. Stuart, and J. C. Tai, *J. Am. Chem. Soc.*, **90**, 2809 (1968).

(9) T. Liljefors and N. L. Allinger, *J. Am. Chem. Soc.*, **98**, 2745 (1976).

(10) N. L. Allinger and J. C. Tai, *J. Am. Chem. Soc.*, **99**, 4256 (1977).

(11) T. Liljefors and N. L. Allinger, *J. Am. Chem. Soc.*, **100**, 1068 (1978).

(12) H. Ziffer and C. H. Robinson, *Tetrahedron*, **24**, 5803 (1968).

(13) R. McDiarmid, *Chem. Phys. Lett.*, **34**, 130 (1975).

(14) A. Galat, J. Koput, and M. Kielczewski, *Bull. Acad. Pol. Sci.*, **25**, 765 (1977); E. Charney, *Tetrahedron*, **21**, 3127 (1965).

(15) A. Yogev, L. Margulies, D. Amar, and Y. Mazur, *J. Am. Chem. Soc.*, **94**, 4558 (1969); A. Yogev, J. Riboid, J. Marero, and Y. Mazur, *ibid.*, **91**, 4559 (1969); G. Aviv, L. Margulis, J. Sagiv, and A. Yogev in Proceedings of the Nobel Workshop in Lund, on Molecular Optical Dichroism and Chemical Applications of Polarized Spectroscopy, Oct 25–27, 1976, B. Norden, Ed., University of Lund, 1977, p 54.

(16) H. G. Kuball, T. Karstens, and A. Schönhofer, *Chem. Phys.*, **12**, 1 (1976); H. G. Kuball, J. Altschuh, R. Kulbach, and A. Schönhofer, *Helv. Chim. Acta*, **61**, 571 (1979); H. G. Kuball, M. Acimis, and J. Altschuh, *J. Am. Chem. Soc.*, in press. However, as shown by the first report on CD of oriented steroids [B. Nordén, *Acta Chem. Scand.*, **26**, 1763 (1972)], such experiments are not without difficulties.

(17) N. L. Allinger and J. T. Sprague, *J. Am. Chem. Soc.*, **95**, 3893 (1973).

(18) A. Davisson and B. Nordén, *Chem. Scr.*, **9**, 49 (1976).

(19) A. F. Moskvin, O. P. Yablonskii, and L. F. Bondar, *Theor. Exp. Chem. (Engl. Transl.)*, **2**, 469 (1966); W. F. Forbes and R. Shilton, *J. Org. Chem.*, **24**, 436 (1959); F. H. Cottee, B. P. Straughan, C. J. Timmons, W. F. Forbes, and R. Shilton, *J. Chem. Soc. B*, 1146 (1967).

(20) K. Inuzuka, *Bull. Chem. Soc. Jpn.*, **34**, 6, 729 (1961).

(21) A. Moscowitz, E. Charney, U. Weiss, and H. Ziffer, *J. Am. Chem. Soc.*, **83**, 4661 (1961); U. Weiss, H. Ziffer, and E. Charney, *Tetrahedron*, **21**, 3105 (1965).

(22) C. Djerassi, R. Records, E. Bunnenberg, K. Mislow, and A. Moscowitz, *J. Am. Chem. Soc.*, **84**, 870 (1962); E. Charney, H. Ziffer, and U. Weiss, *Tetrahedron*, **21**, 3121 (1965).

(23) W. Hug and G. Wagniere, *Helv. Chim. Acta*, **54**, 633 (1971).

(24) The formula has been derived [B. Norden, *Chem. Scr.*, **7**, 226 (1975)] for the antisymmetric coupling mode of two interacting identical electric dipole transitions, but should qualitatively describe also the present intrinsically dissymmetric chromophore; R_B corresponds to the long-wavelength transition (with B symmetry) in butadiene and acrolein.

(25) G. A. Lane and N. L. Allinger, *J. Am. Chem. Soc.*, **96**, 5825 (1974), and references cited therein.

(26) A. W. Burgstahler and R. C. Barkhurst, *J. Am. Chem. Soc.*, **92**, 7601 (1970); A. W. Burgstahler, L. O. Weigel, and J. K. Gawronski, *ibid.*, **98**, 3015 (1976).

(27) E. W. Thulstrup, M. Vala, and J. H. Eggers, *Chem. Phys. Lett.*, **7**, 31 (1970); J. Michl and E. W. Thulstrup, *Spectrosc. Lett.*, **10**, 401 (1977); J. Michl, E. W. Thulstrup, and J. H. Eggers, *J. Phys. Chem.*, **74**, 3878 (1970); E. W. Thulstrup and J. Michl, *J. Am. Chem. Soc.*, **98**, 4533 (1976).