(1 H, m), 4.74 (1 H, d, J = 6), 5.32–5.60 (2 H, m); IR 3600, 1950, 1860 cm^{-1}; MS, m/e 330, 312, 274, 246. The above complex (1.35 g, 4.07 mmol) was acetylated with acetic anhydride (3 mL) and (N,N-dimethylamino)pyridine (200 mg) in pyridine (20 mL) under the above-mentioned condition. Usual workup gave the complex **21** (1.44 g, 95%): mp 76 °C; ^{1}H NMR 0.87 (3 H, d, J = 7), 0.92 (3 H, d, J = 7), 1.70–2.30 (1 H, m), 2.11 (3 H, s), 2.15 (3 H, s), 3.71 (3 H, s), 4.86 (1 H, d, J = 7), 5.10–5.45 (3 H, m); IR 1960, 1870, 1730 cm^{-1}. Anal. Calcd for $C_{17}H_{20}O_6Cr$: C, 54.84; H, 5.41. Found: C, 54.85, H, 5.45.

Preparation of 22 from 21. To a solution of the complex **21** (850 mg, 2.28 mmol) and ethyl 2-(trimethylsilyl)-3-butenoate (2.2 g, 11.8 mmol) in dry CH_2Cl_2 (50 mL) was added boron trifluoride (1.8 mL, 6.9 mmol) at −78 °C under argon. The mixture was stirred at 0 °C for 2 h and warmed to room temperature for 2 h. After addition of water, the reaction mixture was extracted with methylene chloride. The extract was washed with saturated $NaHCO_3$ and brine and dried over $MgSO_4$. Evaporation in vacuo and purification by SiO_2 chromatography gave the coupling product as yellow oil (643 mg, 66%): ^{1}H NMR 0.85 (3 H, d, J = 7), 0.97 (3 H, d, J = 7), 1.30 (3 H, t, J = 7), 1.80–2.20 (1 H, m), 2.13 (3 H, s), 2.30–2.75 (3 H, m), 3.76 (3 H, s), 4.17 (2 H, q, J = 7), 4.82 (1 H, d, J = 6.5), 4.99 (1 H, br s), 5.38 (1 H, d, J = 6.5), 5.89 (1 H, d, J = 16), 6.78–7.15 (1 H, m); IR 1950, 1860, 1700 cm^{-1}; MS, m/e 426, 342. A mixture of the above coupling product (500 mg, 1.17 mmol) and PtO_2 (20 mg) in ethyl acetate (15 mL) was stirred at room temperature under a hydrogen atmosphere for 4 h. Filtration, evaporation, and purification by SiO_2 chromatography gave the complex **22** (485 mg, 97%): mp 80 °C; ^{1}H NMR 0.82 (3 H, d, J = 7), 0.92 (3 H, d, J = 7), 1.26 (3 H, t, J = 7), 1.50–2.00 (4 H, m), 2.11 (3 H, s), 2.10–2.55 (4 H, m), 3.78 (3 H, s), 4.11 (2 H, q, J = 7), 4.82 (1 H, d, J = 6.5), 5.08 (1 H, br s), 5.37 (1 H, d, J = 6.5). Anal. Calcd for $C_{21}H_{28}O_6Cr$: C, 58.87; H, 6.59. Found: C, 58.88; H, 6.70.

Reaction of 22 with Me_2AlNH_2 To Give Complex 23. Dimethylaluminum amide was prepared from Me_3Al (8.0 mL, 19% in hexane, 14 mmol) in dry CH_2Cl_2 (6.0 mL) and anhydrous NH_3 (10 mL) according to the literature method.[18] A solution of the compound **22** (130 mg, 0.31 mmol) in dry xylene (5.0 mL) was added to the dimethylaluminum amide prepared above, and the reaction mixture was refluxed for 4 h under argon. After being quenched with MeOH, the mixture was extracted with ether, and the extract was washed with dilute HCl and brine and dried over $MgSO_4$. Evaporation in vacuo and purification by SiO_2 chromatography gave the nitrile complex **23** (53 mg, 45%) as first fraction: mp 92 °C; ^{1}H NMR 0.86 (3 H, d, J = 7), 0.95 (3 H, d, J = 7), 1.70–2.00 (5 H, m), 2.11 (3 H, s), 2.25–2.60 (3 H, m), 3.77 (3 H, s), 4.80 (1 H, d, J = 7), 5.01 (1 H, br s), 5.38 (1 H, d, J = 7); IR 2250, 1950, 1850 cm^{-1}. Anal. Calcd for $C_{19}H_{23}O_4NCr$: C, 59.84; H, 6.08; N, 3.69. Found: C, 59.83; H, 6.15; N, 3.63. The second fraction gave the amide complex **24** (25 mg, 20%): ^{1}H NMR 0.80 (3 H, d, J = 7), 0.95 (3 H, d, J = 7), 1.40–2.40 (8 H, m), 2.10 (3 H, s), 3.75 (3 H, s), 4.82 (1 H, d, J = 7), 5.09 (1 H, br s), 5.34 (1 H, d, J = 7), 5.15–5.50 (2 H, br); IR 3200–3400, 1960, 1860, 1670 cm^{-1}; MS, m/e 315 ($M^+ - 3CO$), 263 ($M^+ - Cr(CO)_3$), 220, 161. The amide complex **24** was converted to the nitrile complex in 47% yield under the above-mentioned procedure.

Acknowledgment. We express appreciation to professor M. F. Semmelhack for supplying ^{13}C NMR data of the complexes **23** and **25** and also to Professor P. E. Kündig for a discussion about the arene transfer reaction with the (naphthalene)chromium complex.

Circular Dichroism of Linearly Conjugated Chromophores

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A series of chiral four to eight π-electron systems of planar linearly conjugated systems has been prepared, and their chiroptical properties have been determined. The effect of changes in both configuration and conformation on the circular dichroism spectra of these molecules is discussed.

Substantial research efforts have been devoted toward the understanding of the chiroptical properties of conjugated dienes and enones. Homoannular *cisoid* dienes constitute a group of dienes with an inherently chiral chromophore for which an empirical diene chirality rule has been proposed.[1] A similar empirical rule has been advanced for skewed *transoid* dienes.[2] Alternatively, allylic axial bonds have been proposed to control long-wavelength π–π* Cotton effect of dienes and enones[3–5] and a diene quadrant rule was postulated to account for the rotatory contributions of the diene and the axial allylic substituents.[6] Recently these different proposals were combined into an empirical-theoretical model of a helical 1,3-cyclohexiadiene chromophore.[7]

There are numerous optically active natural products which contain planar (or nearly planar) polyunsaturated conjugated chromophores. Examples of which are the triene chromophore in leukotrienes (**1a**), the polyene chromophore in optically active carotenoids (**1b**), and the conjugated carbonyl chromophore in the trichothecenes (**1c**) and the macrolide antibiotics (**1d**).

With the exception of the carotenoids[8] there has been only a paucity of effort directed toward the understanding of the chiroptical effects of these types of chromophores

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[†] Visiting Professor from Department of Chemistry, A. Mickiewicz University, Poznan, Poland.

(1) Moscowitz, A.; Charney, E.; Weiss, U.; Ziffer, H. *J. Am. Chem. Soc.* **1961**, *83*, 4661. Burstahler, A. W.; Ziffer, H.; Weiss, U. *Ibid.* **1961**, *83*, 4660.

(2) Charney, E.; Ziffer, H.; Weiss, U. *Tetrahedron* **1965**, *21*, 3121.

(3) Burgstahler, A. W.; Barkhurst, R. C. *J. Am. Chem. Soc.* **1970**, *92*, 7601. Burgstahler, A. W.; Barkhurst, R. C.; Gawronski, J. K. In *Modern Methods of Steroid Analysis*; Heftmann, E., Ed.; Academic Press: New York, 1973.

(4) Burgstahler, A. W.; Weigel, L. O.; Gawronski, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 3015.

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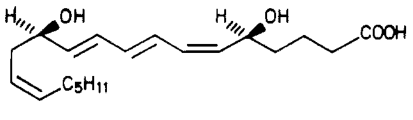
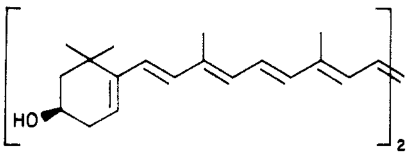
(8) See, for example: Sturzenegger, V.; Buchecker, R.; Wagnière, G. *Helv. Chim. Acta* **1980**, *63*, 1074.

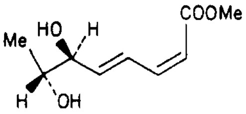
0022-3263/86/1951-2863$01.50/0 © 1986 American Chemical Society



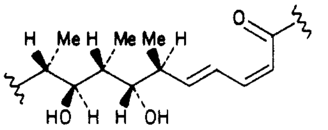
(**1a**) leukotriene-B4



(**1b**) zeaxanthin

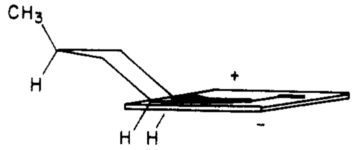


(**1c**) octadienic ester fragment in trichothecenes



(**1d**) fragment of rifamycin B ansa bridge

in natural products. It was not until recently that an attempt was made in this direction by applying an empirical "planar diene rule", which had been proposed for



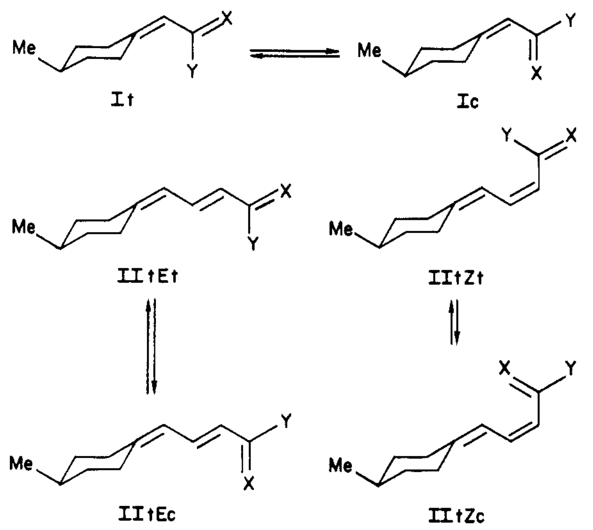
planar exocyclic transoid dienes and α,β-unsaturated aldehydes, to a number of dihydrotachysterols.[9] This rule related the sign of the long-wavelength $\pi-\pi^*$ Cotton effect to the *absolute configuration* of the molecule.

In order to arrive at any understanding of the chiroptical properties of these chromophores, a fundamental question needs to be addressed. This concerns the effect that the *geometry of the planar π-system* has on the chiroptical properties of molecules which possess chiral perturbers of the same absolute configuration. In this connection it has been suggested that the sign of the "allylic axial substituent effect" is related to the diene cis/trans geometry.[10] It has also recently been shown[11] that the opposite sign Cotton effects are observed for the transoid and cisoid conformers of the triene chromophore in tachysterol$_3$.

Our aim was to determine whether, in fact, the chiroptical properties of planar conjugated chromophores are dependent on their overall geometry, i.e., their configuration and conformation. To avoid complications arising from complex equilibria in acyclic systems, we have selected the 4-methylcyclohexylidene group as the chiral substituent to which the π-chromophores will be attached. It is known that in the (4-methylcyclohexylidene)propene case the 4-methyl substituent exists at room temperature at least 95% in a conformation with the methyl group in an equatorial position.[9a]

It was anticipated that the extension of the π-chain would produce not only *E* and *Z* configurational isomers but also transoid and cisoid conformers. Which conformer would predominate at equilibrium would depend on the size of the X and Y groups (Scheme I).

Scheme I



Scheme II

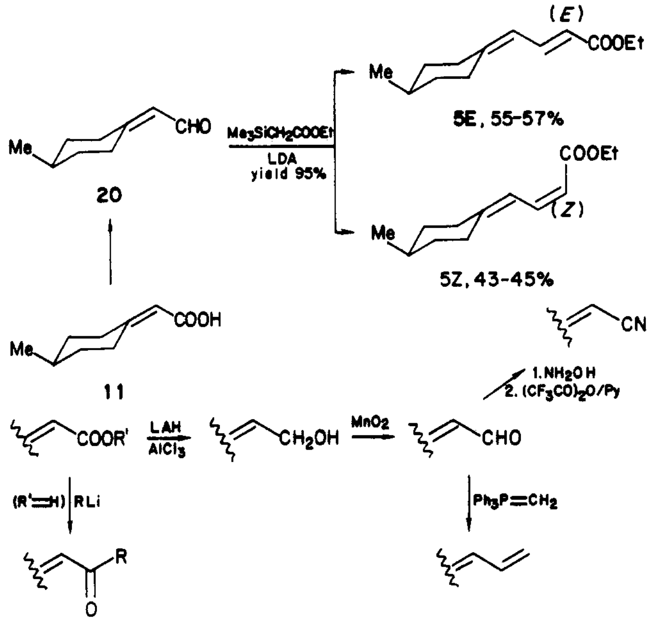
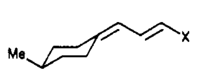


Table I. Effect of C=C Bond Configuration on CD

		 *E*		 *Z*	
		CD	UV	CD	UV
	X	$\Delta\epsilon$ (λ, nm)	λ (nm) (ϵ)	$\Delta\epsilon$ (λ, nm)	λ_{max}(nm) (ϵ)
2	CHO	+0.3 (277)	278 (34 700)	−0.4 (289)	287 (22 000)
3	COMe	+1.2 (287)	281 (30 500)	−1.4 (290)	291 (19 700)
4	CO-*t*-Bu	+1.6 (287)	287 (26 100)		
5	COOEt	+0.6 (273)	271 (30 600)	−4.8 (275)	275 (27 300)
6	CN	ca >0	266 (34 200)	−5.2 (268)	268 (28 900)
7	CH=CH$_2$	−4.1 (275)	275 (54 000)	−0.5 (276)	275 (38 600)

Whereas predominance of the transoid conformation of I and II would be expected for the dienes and trienes when X = CH$_2$ and Y = H, a cisoid conformation might be anticipated for I and II when X is a small substituent like an oxygen atom and Y is large such as an alkyl group. Thus the chromophore will be related to both the config-

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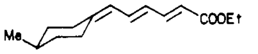
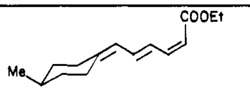
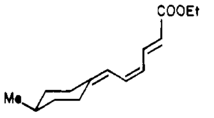
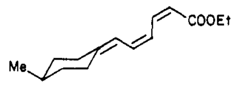
[9] (a) Duraisamy, M.; Walborsky, H. M. *J. Am. Chem. Soc.* **1983**, *105*, 3264. (b) Duraisamy, M.; Walborsky, H. M. *Ibid.* **1983**, *105*, 3270.

[10] Gawronski, J.; Gawronska, K. *J. Chem. Soc., Chem. Commun.* **1980**, 346.

[11] Maessen, P. A.; Jacobs, H. J. C.; Carnelisse, J.; Havinga, E. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 718.

Table II. Effect of C═C Bond Configuration in Trienoic Esters (8) on CD

 (*E*,*E*) $\Delta\epsilon$ (λ) ca. 0 ϵ, λ_{max} 48 800 (308 nm)	 (*Z*,*E*) -5.3 (314 nm) 39 000 (314 nm)
 (*E*,*Z*) $\Delta\epsilon$ (λ) -0.65 (308 nm) ϵ, λ_{max} 38 800	 (*Z*,*Z*) -0.5 (305 nm) 33 100 (314 nm)

uration and conformation of the π-bond.

Synthesis. The stereoselective construction of functionalized carbon–carbon double bonds can be achieved by use of the Wittig or Horner–Emmons type of reactions.[12] Since both the *E* and *Z* olefinic products were desired, the method of choice was the high yield, nonracemizing condensation of the carbonyl compound with lithio(trimethylsilyl)acetates[13] which are known to produce a mixture of *Z* and *E* isomers which are rich in *Z*.[14]

The basic synthetic sequences involved in the preparation of the target compounds are outlined in Scheme II. The aldehyde **20**, prepared from (4-methylcyclohexylidene)acetic acid (**11**) of known absolute configuration and optical purity[15] was condensed with ethyl (trimethylsilyl)acetate anion to give a mixture of dienoic esters (5*E*/5*Z* = 56:44) in high yield. The ester mixture was easily separated by chromatography on silica gel and they served as intermediates for the preparation of other functional groups (Scheme II) by using reactions that are known not to cause any racemization of the substrate or product.

Configurational *E*/*Z* Effect. CD data on the *E* and *Z* isomers are presented in Tables I and II. It is seen that geometric isomers differ in sign (**2**, **3**, **5**) or magnitude (**5**, **7**) of the π-π* Cotton effect (Table I). With the exception of the trienes **7**, *E* isomers show a more positive Cotton effect when compared to the *Z* isomers. In addition, *Z* isomers exhibit low ϵ_{max} coefficients as well as a small red shift of the UV max. Trienes **7E** and **7Z** differ in magnitude of the π-π* Cotton effect and ϵ_{max}, but their absorption maxima fall into the same wavelength region. This has also been observed in the UV spectra of *cis*- and *trans*-hexatriene.[16] In addition, stereoisomeric trienoic esters **8** (Table II) show interesting variations in the intensity of the Cotton effect. The **8Z,E** isomer gives a strong negative Cotton effect comparable in magnitude to that of the **5Z** ester. The **8E,Z** and **8Z,Z** isomers give small negative Cotton effects while the **8E,E** shows no measurable Cotton effect. UV maxima for esters **8** show a familiar pattern of decreasing ϵ_{max} with increasing number of *Z* bonds, as well as a red shift for each pair of *E*,*E*/*Z*,*E* and *E*,*Z*/*Z*,*Z* isomers.

Scheme III

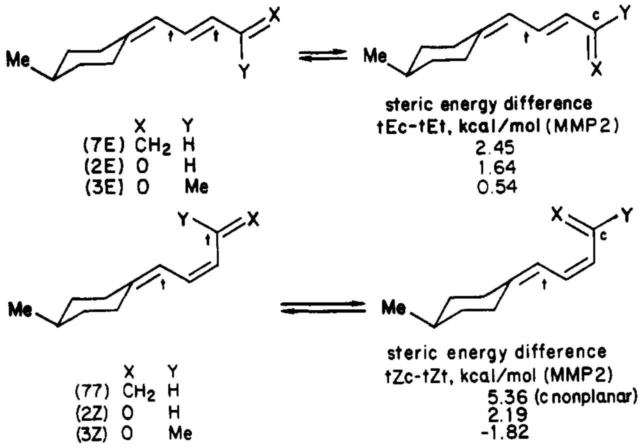
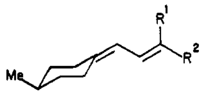


Table III. CD Data on α,β-Unsaturated Carbonyl Compounds

		
	X	$\Delta\epsilon$ (nm)
9	CN	+1.4 (215)
10	COO⁻(MeOH)	+2.6 (232)
11	COOH	+3.3 (220)
12	COOMe	+2.9 (218)
13	COMe	+2.9 (235)
14	CO-*t*-Bu	+2.7 (237)

Table IV. CD Data on the Dienes and Related Compounds

			
	R^1	R^2	$\Delta\epsilon$ (nm)
15	H	H	-3.7 (238)
16	H	CH_2OH	-4.2 (238)
17	CH_2OH	H	-5.4 (244)
18	H	CMe_2OH	-3.0 (241)
19	CMe_2OH	H	-4.1 (241)

		
	X	$\Delta\epsilon$ (nm)
20	O	-2.1 (230)
21	NOH (anti)	-1.7 (224)
22	NOH (syn)	-5.0 (231)

Conformational t/c Effect. In order to evaluate the importance of transoid/cisoid conformational equilibria (Scheme I), we have calculated for selected molecules steric energy differences between the respective lowest energy conformers using Allinger's MMP2 program.[17] In all cases, with the exception of **7Z** cisoid, the calculated low-energy conformation had a planar π-electron framework. A strong preference for a transoid conformation (>95%) was calculated for the trienes **7E** and **7Z**, and to the extent of >90% for the aldehydes **2E** and **2Z** (Scheme III). However, for the methyl ketone **3E** the equilibrium conformation was only ca. 70% in favor of transoid and for the **3Z** isomer there was clearly a strong preference for the

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(12) For reviews, see: (a) Schlosser, M. *Top. Stereochem.* **1970**, *5*, 1. (b) Gosney, I.; Rowley, A. G. In *Organophosphorous Reagents in Organic Synthesis*; Cadogan, J. I. G., Ed.; Academic Press: New York, 1979. (c) Bestmann, H. J.; Vostrowsky, O. *Top. Current Chem.* **1983**, *109*, 85. See also: Maryanoff, B. E.; Reitz, A. B.; Duhl-Emswiler, B. A. *J. Am. Chem. Soc.* **1985**, *107*, 217. Minami, N.; Ko, S. S.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 1109. Still, W. C.; Gennari, C. *Tetrahedron Lett.* **1983**, *24*, 4405.

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(14) Tulshian, D. B.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1981**, *103*, 474.

(15) Duraisamy, M.; Walborsky, H. M. *J. Am. Chem. Soc.* **1983**, *105*, 3252.

(16) McDiarmid, R.; Sabljic, A.; Doering, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 826.

(17) For the use of Allinger's force field method for calculation of the conformational energies of conjugated dienes, α,β-unsaturated aldehydes, and ketones, see: Liljefors, T.; Allinger, N. *J. Am. Chem. Soc.* **1976**, *98*, 2745. Allinger, N. L.; Tai, S. C. *J. Am. Chem. Soc.* **1977**, *99*, 4256. Tai, J. C.; Allinger, N. L. *Tetrahedron* **1981**, *37*, 2755 and ref 9a therein.

Table V. IR Stretching Bands for Selected α,β-Unsaturated Carbonyl Compounds

ν(>C=CH—)	ν(—$H_\beta C=C_\alpha H$—)	ν(C=O)	rel integrtd intensity $C=O/C_\alpha=C_b$
aldehydes			
(**20**) 1630 m		1675 s	2.1
(**2E**) 1630 s	1570 w	1680 s	2.3
(**2Z**) 1630 m	1570 w	1665 s	2.2
methyl ketones			
(**13**) 1620 s		1680 s-m	0.87
(**3E**) 1625 s	1585 s	1670 s	1.1
(**3Z**) 1620 s	1570 s	1680 s	0.85
tert-butyl ketones			
(**14**) 1650 s		1680 s-m	0.80
(**4E**) 1625 m	1585 s	1670 m	0.68

cisoid conformation (>95%).

It is clear that conformational changes do have an effect on the CD spectra of planar chromophores. Within each group of *E* and *Z* isomers shown in Table I there are differences in the intensity of the Cotton effects (see carbonyl compounds **2**, **3**, and **4**). Also the *E* series of carbonyl compounds (**2–5**) display Cotton effect of opposite sign to that of triene **7E**. Remarkable is the similarity of the CD maxima between the esters **5** and nitriles **6**. Nitriles, due to the symmetry of the CN group, cannot be considered in terms of t/c conformation. Although MMP2 calculations on esters are lacking, it is expected that the esters will show a less marked preference for either a cisoid or transoid conformation.[28] The IR[18] and ^{1}H NMR spectra of acrylates have been interpreted in terms of a predominating cisoid conformation when there are no substituents on the α-carbon and no alkyl substituent in the cis β-position. Moreover, the cisoid–transoid equilibrium appears to be solvent-dependent.[20] INDO[21] and CNDO[22] calculations on acrylates do not give a conclusive picture but IR and Raman studies show that the transoidal conformation is the low-energy conformer.[23]

Further evidence for a conformational effect is found in Tables III and IV; with the exception of aldehyde **20**, α,β-unsaturated carbonyl and cyano compounds (**9–14**) show a significant positive π–π* Cotton effect, while dienes **15–19** (Table IV) show a strong negative Cotton effect regardless of the substitution by nonconjugated groups. Similarly, a negative Cotton effect is also displayed by aldehyde **20** and its oxime isomers **21** and **22** (negative Cotton effect is predicted for dienes **15–19** and aldehyde **20** on the basis of the "planar diene rule"[9]). Thus, a negative Cotton effect can be attributed to the transoid chromophore while a positive Cotton effect can be ascribed to the cisoid (or cisoid-like as in the case of nitrile **9**) chromophore in the absolute configurations shown.

The experimental indication of transoid/cisoid conformational changes in carbonyl compounds can be found in IR and ^{1}H NMR spectra. It has been established[24] that the ratio of the integrated intensities of the C=O and the conjugated C=C stretching frequencies can provide information concerning the conformation of the C=CC=O chromophore. A ratio of (C=O/C=C) of <2.0 (typically ca. 1.4) is indicative of cisoidal conformation whereas a ratio greater than 2.0 (typically ca. 5.2) is indicated of a transoidal conformation. Table V lists positions and relative integrated intensities of the C=O and C=C bands in aldehydes **2** and **20** and ketones **3**, **4**, **13**, and **14**. While in aldehydes **2** the stretching band for disubstituted C=C bond is much weaker compared to C=O stretch, it is of comparable intensity in methyl ketones **3** and even more intense than C=O stretch in *tert*-butyl ketone **4E**. A similar increase of intensity of the trisubstituted C=C stretch is found in methyl and *tert*-butyl ketones **13** and **14** when compared to aldehyde **20**. Figure 1 features the C=O and C=C portion of the IR spectrum for the ketone **4E**.

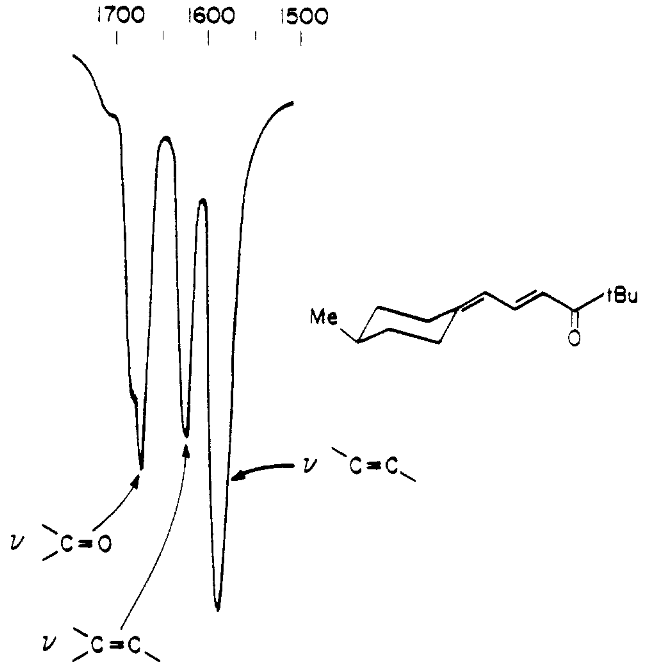

Figure 1.

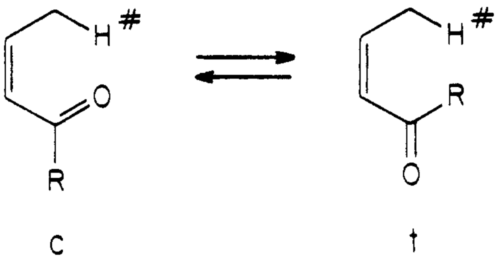

Figure 2.

Table VI. ^{1}H NMR Shift Differences of the Vinyl Protons H_β and H_α

	X	$\Delta\delta(Z\text{-}E)$, ppm H_β	$\Delta\delta(Z\text{-}E)$, ppm H_α
(7)	$CH=CH_2$	−0.24	0.43
(6)	CN	−0.18	0.42
(2)	CHO	−0.17	0.74
(5,8)	COOEt	−0.70, −0.64, −0.73	1.23, 1.13, 1.22
(3)	COMe	−0.71	1.21
(4)	CO-*t*-Bu	−0.80	1.23

The chemical shift of the proton H# in the arrangement shown in Figure 2 should be sensitive to the presence of the cisoid conformation. Indeed, the data of Table VI show

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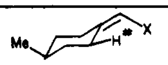
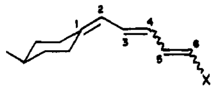
Table VII. ^1H NMR Shift of the Allylic *Z*-Equatorial Proton $H^\#$



	X	ppm
(15)	$CH{=}CH_2$	2.78
(9)	CN	2.90
(20)	CHO	3.33
(12)	COOMe	3.75
(13)	COMe	3.69
(14)	CO-*t*-Bu	3.58

Table VIII. ^{13}C NMR Data on Side Chain sp^2-Carbon Atoms



No.	C1	C2	C3	C4	C5	C6	X
2E	157.05	121.19	148.00	129.98			195.98
2Z	156.11	116.31	142.38	125.32			190.83
3E	155.30	121.06	139.03	128.39			198.83
3Z	156.14	119.51	137.75	122.42			199.28
4E	155.03	121.24	138.70	122.07			204.98
5E	153.87	120.64	140.42	118.91			167.76
5Z	154.22	118.86	139.88	115.10			166.97
6E	155.32	95.82	146.21	120.38			119.03
6Z	155.60	94.20	144.73	119.31			117.06
7E	144.65	122.10	129.32	131.06	137.58	115.56	
7Z	145.02	117.36	132.35	125.52	127.63	116.97	
8E,E	149.66	119.30	136.82	127.77	145.31	122.14	167.34
8E,Z	149.30	117.44	132.72	124.13	139.53	120.56	167.38
8Z,E	149.47	122.63	137.60	126.74	145.37	115.66	166.71
8Z,Z	149.29	116.74	132.71	122.21	138.89	116.78	166.67
9	168.36	92.12					116.98
12	163.29	112.62					167.03
13	161.40	121.51					199.19
14	161.04	117.23					207.08
15	143.54	122.91	132.80	114.47			
16	144.13	121.16	127.79	129.35			
17	145.60	116.51	126.46	127.08			
20	167.59	125.34					190.48

that the difference of chemical shift between *Z* and *E* configurational isomers for the protons H_β and H_α is larger on going from aldehyde **2** to the ketones **3** and **4** and the esters **5** and **8**. The difference is even more substantial for H_α when compounds **3–5** and **8** are compared to **6** and **7**. Similar deshielding of the proton $H^\#$ by the carbonyl group of the ketones **13** and **14** and ester **12** (compared to aldehyde **20**, nitrile **9**, or diene **15**) is seen in the data of Table VII. ^{13}C NMR data on the side-chain sp^2 carbon atoms can be found in Table VIII (see Experimental Section).

Discussion

It is evident from the results presented that for molecules of fixed absolute configuration the observed π–π^* Cotton effect can be of either sign and varying magnitude depending on the geometry of the (planar) chromophore. For practical application it would be desirable if this dependence could be formulated into a simple structure–observed effect relationship. Although no empirical rule based on symmetry can be offered, our results can be rationalized on the basis of two-group electric dipole mechanism.[25] The long-wavelength π–π^* transition is polarized along the long axis of the planar chromophore. The interaction of the electric-dipole transition moment (μ_1) with the electric dipole (μ_2) induced in the ring C–C bonds gives the necessary non-zero magnetic moment component to produce nonvanishing rotational strength, proportional to $[R_{21}\cdot\mu_{02} \times \mu_{01}]$. Thus, any change in the direction of μ_1 with regard to the chirally substituted ring will change the magnitude or sign of the rotational strength.

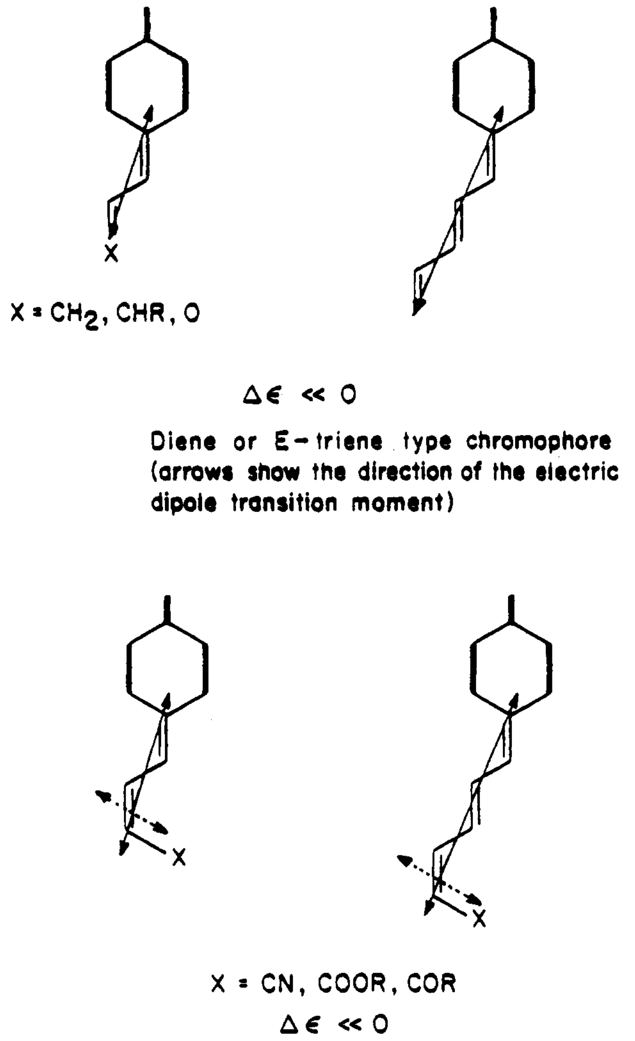


Figure 3.

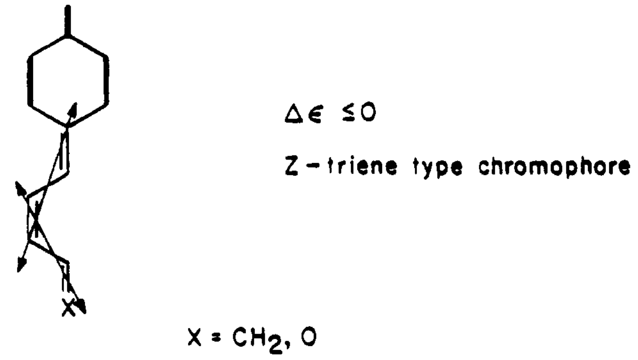


Figure 4.

The three categories of chromophores are shown in Figures 3–5.

Compounds with a transoid or *E*-transoid chromophore are referred to as diene or *E*-triene type and they display a strong negative Cotton effect (Figure 3). To this group belong **7E** and **15–22**. The diminished intensity of the aldehyde **20** and anti-oxime **21** Cotton effect may be a

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(25) Mason, S. F. *Molecular Orbital Activity and the Chiral Discriminations*; Cambridge University Press: Cambridge, 1982.

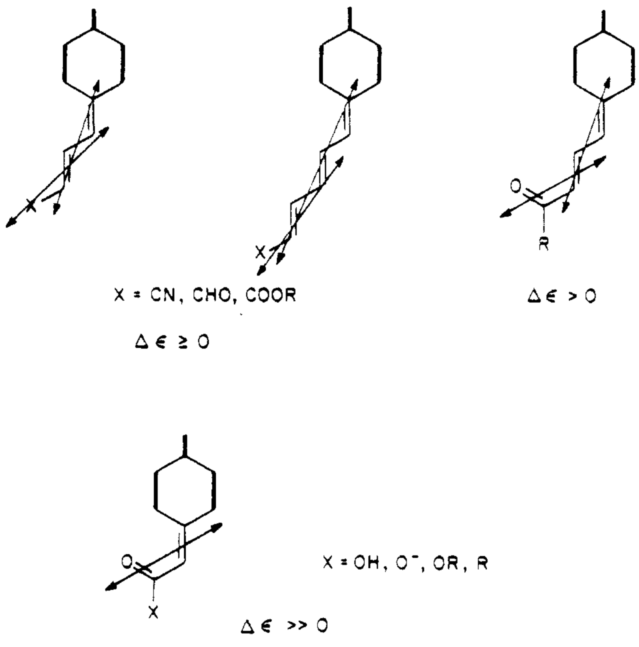
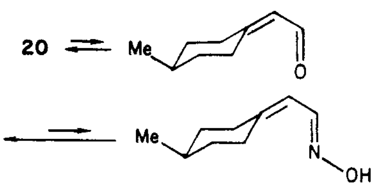


Figure 5.

reflection of the small contribution from the cisoid conformers:



Such a cisoid conformation would not be likely with the syn isomer (22) due to unreasonably high energy. Moreover, it now becomes apparent that compounds with a terminal polar group in a *Z* configuration (**3Z**, **5Z**, **6Z**, and **8Z,E**) also fall into the same category. The broken arrow in Figure 3 indicates that the effect of such groups on the rotational strength of π–π^* dienoic or trienoic chromophore to which it is attached is very small.

Compounds with a *Z*-triene type chromophore (**2Z** and **7Z**) show small negative Cotton effects (Figure 4). This is to be expected as the overall electric-dipole transition moment direction is now close to the symmetry plane of the 4-methylcyclohexylidene ring which then makes the magnetic-dipole transition moment nearly vanishing. As in the case of the **8Z,Z** compound, **8Z,Z** shows that the terminal ester group does not change the rotational strength of the parent *Z*-triene system. This may also be the case with the **8E,Z** isomer.

Polar chromophoric groups conjugated in the *E* configuration belong to the third class of chromophores (Figure 5). Here the measured π–π^* Cotton effect is positive to the degree that is dependent on the extent to which the cisoid conformation of the terminal group contributes and the distance of the terminal group from the chiral ring. Thus Cotton effects of very low intensity are observed for nitrile **6E**, aldehyde **2E**, and esters **5E** and **8E,E**. More intense positive Cotton effects are displayed by ketones **3E** and **4E** as well as by nitrile **9**. Large Cotton effects are characteristic of carbonyl compounds **10**–**14**.

In summary, it has been demonstrated that both configuration and conformation have significant effects on the chiroptical properties of molecules possessing linearly conjugated chromophores.

Experimental Section

Melting points were determined with a Mel-Temp apparatus and are uncorrected. Infrared (IR) spectra were measured with Perkin-Elmer Model 257 grating spectrophotometer using the polystyrene 1601 cm^{-1} band for calibration. Nuclear magnetic resonance (NMR) spectra were recorded on Brucker 200-MHz or 270-MHz spectrometers. The solvent used was $CDCl_3$, unless noted otherwise, with Me_4Si as internal standard. Mass spectra (MS) were obtained with a Finnigan high resolution instrument. The microanalyses were performed by Beller Laboratories, Göttingen, Germany.

Optical rotations were measured at the 546.1-nm mercury line on a Bendix-Ericson Model 987 ETL/NPL polarimeter with a Bendix Model DR-L digital display. The accuracy was ±0.002° and the cell length was 0.4 dm. Ultraviolet (UV) spectra were recorded with a Cary 219 spectrophotometer. Circular dichroism (CD) spectra were recorded with a JASCO Model J-500C spectrophotometer. The CD data have been corrected for the optical purities of the samples. The solvent used for UV and CD measurements was spectrograde cyclohexane, unless noted otherwise. For column chromatography 70–230 mesh silica gel (Merck) was used unless noted otherwise. Radial chromatography thin-layer separations were performed with Merck silica gel 60 PF_{254} using a Harrison Research Chromatotron Model 7924T. Qualitative GLPC analyses were performed on a 5710A Hewlett-Packard gas chromatograph equipped with thermal conductivity detector using helium as carrier gas and 15% SE-30 on acid-washed 80/100 Chromosorb P, 10 ft × $^1/_8$ in. column. For reagents and solvents purification, see ref 12. Synthesis of compounds **11**, **12**, **15**, and **20** was reported in ref 12. The enantiomeric excess of the starting acid **11**, and hence all compounds derived from it, was 90%.

Ethyl (*E*)- and (*Z*)-4-((*aS*)-4-Methylcyclohexylidene)-2-butenoates (5E and 5Z). A solution of lithium diisopropylamide, prepared at 0 °C from 2.2 mL (16 mmol) of diisopropylamine, 6.4 mL of 2.5 M *n*-butyllithium in hexane, and 40 mL of THF, was cooled to −75 °C and treated with 2.9 mL (16 mmol) of ethyl (trimethylsilyl)acetate. After 30 min a solution of the aldehyde **20**, 1.75 g (12.6 mmol), in 5 mL of THF was added dropwise. The solution was allowed to warm to room temperature (2 h) and then quenched with water. Extractive workup with hexane and 2 N HCl gave a crude product which was redissolved in hexane and filtered through alumina using hexane as solvent. After removal of solvents there was obtained 2.5 g (95%) of a mixture of esters **5E** and **5Z**; GLPC at 200 °C gave a ratio **5E**:**5Z** = 57:43. The esters were separated by radial chromatography using hexane–5% diethyl ether as eluent, the **5Z** isomer being less polar.

On a 4 times larger scale the products were obtained in 55:45 ratio and separated by column chromatography on alumina. The **5Z** isomer was eluted with hexane (yield 34%), **5E** isomer was eluted with hexane–2% diethyl ether (yield 36%).

5E: $[\alpha]^{25}_{546}$ + 48.3° (*c* 0.8, cyclohexane); IR (film) 2960, 2840, 1710, 1640, 1615, 1280, 1170, 1150; ^1H NMR 0.91 (d, *J* = 7 Hz, 3 H), 0.9–2.4 (m, 8 H), 1.30 (t, *J* = 7 Hz, 3 H), 2.90 (br d, *J* = 12 Hz, 1 H), 4.20 (q, *J* = 7 Hz, 2 H), 5.79 (d, *J* = 15 Hz, 1 H), 5.94 (d, *J* = 11.5 Hz, 1 H), 7.62 (dd, *J* = 15, 11.5 Hz, 1 H); UV 30600 (271 nm); CD (Δε) +0.6 (273 nm). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.08; H, 9.84.

5Z: $[\alpha]^{25}_{546}$ −127.8° (*c* 0.5, cyclohexane); IR (film) 3050 (w), 2960, 2850, 1710, 1630, 1590, 1200, 1170, 1045, 835; ^1H NMR 0.92 (d, *J* = 7 Hz, 3 H), 0.95–2.3 (m, 7 H), 1.30 (t, *J* = 7 Hz, 3 H), 2.39 (br d, *J* = 12 Hz, 1 H), 2.85 (br d, *J* = 12 Hz, 1 H), 4.19 (q, *J* = 7 Hz, 2 H), 5.57 (d, *J* = 11.5 Hz, 1 H), 6.92 (t, *J* = 11.5 Hz, 1 H), 7.17 (d, *J* = 11.5 Hz, 1 H); UV (ε) 27300 (275.1 nm); CD (Δε −4.8 (275 nm), −2.1 (210 nm). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.04; H, 9.76.

(*E*)- and (*Z*)-4-((*aS*)-4-Methylcyclohexylidene)-2-butenenitriles (6E and 6Z). Sodium hydride (0.25 g, 50% in oil, 5 mmol) was washed under nitrogen with pentane. Dry dimethoxyethane (5 mL) was added, followed by diethyl (cyanomethyl)phosphonate (0.81 mL, 5 mmol). After 30 min, the solution was cooled to 0 °C and a solution of the aldehyde **20**, 0.61 g (4.4 mmol), in 2 mL of DME was added dropwise. After 1 h at room temperature the solution was worked up as previously described in the preparation of **5E** and **5Z** to give 0.48 g of colorless oil which was shown to be a 4:1 mixture of **6E** and **6Z** by GLPC. The isomeric nitriles were separated by radial chromatography (hexane).

6E: $[\alpha]^{25}{}_{546}$ +54.5° (*c* 0.9, cyclohexane); IR (film) 3040 (w), 3010 (w), 2920, 2840, 2230, 1635, 1590, 1460, 980; ^{1}H NMR 0.92 (d, J = 7 Hz, 3 H), 0.95–2.4 (m, 8 H), 2.76 (br d, J = 12 Hz, 1 H), 5.22 (d, J = 15 Hz, 1 H), 5.91 (d, J = 11.5 Hz, 1 H), 7.31 (dd, J = 15, 11.5 Hz, 1 H); UV (ϵ) 34 200 (266 nm); CD $\Delta\epsilon \geq 0$ at UV$_{\max}$. Anal. Calcd for $C_{11}H_{15}N$: C, 81.95; H, 9.37; N, 8.68. Found: C, 81.93; H, 9.37; N, 8.60.

6Z: $[\alpha]^{25}{}_{546}$ −178.2° (*c* 0.3, cyclohexane); IR (film) 3060 (w), 2960, 2850, 2235, 1635, 1580, 1460, 1250, 765; ^{1}H NMR 0.94 (d, J = 7 Hz, 3 H), 0.95–2.30 (m, 7 H), 2.38 (br d, J = 12 Hz, 1 H), 2.76 (br d, J = 12 Hz, 1 H), 5.08 (d, J = 11.5 Hz, 1 H), 6.33 (d, J = 11.5 Hz, 1 H), 7.13 (t, J = 11.5 Hz, 1 H); UV (ϵ) 28 900 (268 nm); CD $(\Delta\epsilon)$ −5.2 (268 nm). Anal. Calcd for $C_{11}H_{15}N$: C, 81.95; H, 9.37; N, 8.68. Found: C, 81.98; H, 9.42; N, 8.64.

(*Z*)-4-((*aS*)-4-Methylcyclohexylidene)-2-buten-1-ol (17). To a solution of 1.7 g of 95% $LiAlH_4$ in 35 mL of diethyl ether was added at 0 °C a solution of 1.86 g of $AlCl_3$ in 25 mL of anhydrous ether. After being stirred at 0 °C for 1 h, a solution of **6Z** (3.4 g) in 25 mL of ether was added dropwise. Stirring was continued for 3 h and the mixture was decomposed carefully with 2 N NaOH. The reaction mixture was filtered and the salts were washed with ether. The combined ether abstracts were washed with saturated NaCl solution and dried over $MgSO_4$, and the solvent was evaporated. The yield of the products, a colorless oil, crystallizing from pentane, was 2.7 g (99%). An analytical sample was purified by radial chromatography with dichloromethane as eluent: $[\alpha]^{25}{}_{546}$ −58.3° (*c* 1, cyclohexane); IR (film) 3300, 3030, 2960, 2850, 1650, 1080–930; ^{1}H NMR 0.91 (d, J = 7 Hz, 3 H), 0.85–2.35 (m, 8 H), 2.76 (br d, J = 12 Hz, 1 H), 4.33 (d, J = 7 Hz, 2 H), 5.52 (dt, J = 11.5, 7 Hz, 1 H), 6.03 (d, J = 11.5 Hz, 1 H), 6.36 (t, J = 11.5 Hz, 1 H); UV (ϵ) 29 000 (244.5 nm); CD $(\Delta\epsilon)$ −5.4 (244 nm), +5.6 (195 nm). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.41; H, 10.98.

(*E*)-4-((*aS*)-4-Methylcyclohexylidene)-2-buten-1-ol (16). This compound was prepared from **6E** in a manner analogous to **17Z**; yield 89%, colorless oil. An analytical sample was purified by radial chromatography (hexane–25% diethyl ether): $[\alpha]^{20}{}_{546}$ −6.1° (*c* 1, cyclohexane); IR (film) 3310, 3025, 2960, 2850, 1660, 1630 (w), 1460, 1100, 1015, 985; ^{1}H NMR 0.90 (d, J = 7 Hz, 3 H), 0.85–2.30 (m, 8 H), 2.75 (br d, J = 12 Hz, 1 H), 4.17 (d, J = 7 Hz, 2 H), 5.73 (dt, J = 15, 7 Hz, 1 H), 5.79 (d, J = 11.5 Hz, 1 H), 6.51 (dd, J = 15, 11.5 Hz, 1 H); UV (ϵ) 30 100 (243 nm); CD $(\Delta\epsilon)$ −4.2 (238), +6.5 (202).

(*E*)-4-((*aS*)-4-Methylcyclohexylidene)-2-butenol (2E). A solution of the dienol **16** (0.5 g) in pentane (40 mL) was stirred under nitrogen in an ice-bath with 3.5 g of manganese dioxide for 2 h. The mixture was filtered and the solution evaporated. The product was purified by radial chromatography (hexane–10% diethyl ether): yield 0.46 g (92%); $[\alpha]^{22}{}_{546}$ +8.1° (*c* 1, cyclohexane); IR (film) 3020 (w), 2960, 2850, 2720, 1680, 1630, 1590, 1460, 1190, 1140, 990, 905; ^{1}H NMR 0.94 (d, J = 7 Hz, 1 H), 0.95–2.45 (m, 8 H), 2.90 (br d, J = 12 Hz, 1 H), 6.10 (dd, J = 15, 8 Hz, 1 H), 6.11 (d, J = 11.5 Hz, 1 H), 7.46 (dd, J = 15, 11.5 Hz, 1 H), 9.57 (d, J = 8 Hz, 1 H); UV 34 700 (278 nm); CD $(\Delta\epsilon)$ −0.04 (408 nm), −0.13 (386 nm), −0.21 (366 nm), −0.22 (350 nm), −0.17 (336 nm), +0.3 (277 nm); MS calcd for $C_{11}H_{16}O$ 164.1201, found 164.1196.

(*Z*)-4-((*aS*)-4-Methylcyclohexylidene)-2-butenol (2Z). Oxidation of **17**, carried out as for preparation of **2E**, afforded an unstable **2Z** in moderate yields (30–50%) after radial chromatography purification (hexane–10% diethyl ether): $[\alpha]^{25}{}_{546}$ −9.8° (*c* 0.9, cyclohexane); IR (film) 3025 (w), 2960, 2850, 2720, 1665, 1625, 1570, 1460, 1245, 1200–950, 790; ^{1}H NMR 0.94 (d, J = 7 Hz, 3 H), 0.95–2.45 (m, 8 H), 2.88 (br d, J = 12 Hz, 1 H), 5.77 (dd, J = 11.5, 8 Hz, 1 H), 6.85 (d, J = 11.5 Hz, 1 H), 7.29 (t, J = 11.5 Hz, 1 H), 10.24 (d, J = 8 Hz, 1 H); UV (ϵ) 22 200 (287 nm); CD $(\Delta\epsilon)$ −0.4 (289 nm); MS calcd for $C_{11}H_{16}O$ 164.1201, found 164.1201.

(*E*)-5-((*aS*)-4-Methylcyclohexylidene)-1,3-pentadiene (7E). To a stirred suspension of 1.45 g (4 mmol) of anhydrous methyltriphenylphosphonium bromide in 16 mL of dry THF, cooled in a dry ice–CCl_4 bath, was added 1.6 mL of 2.5 M *n*-BuLi in hexane. After being stirred for 0.5 h, a solution of the aldehyde **2E** (0.38 g, 2.3 mmol) in 4 mL THF was added. The reaction mixture was allowed to warm to room temperature (1 h) and was quenched with wet ether and water. Extraction with pentane gave a yellow crude product which was purified by radial chromatography (pentane) to give 0.25 g (67%) of a colorless oil, $[\alpha]^{25}{}_{546}$ −58.8° (*c* 1, cyclohexane); IR (film) 3060 (w), 3010 (w), 2940, 2905, 2840, 1640 (w), 1620, 1580 (w), 1460, 1005, 950, 895; ^{1}H NMR 0.90 (d, J = 7 Hz, 3 H), 0.85–2.30 (m, 8 H), 2.75 (br d, J = 12 Hz, 1 H), 5.01 (dd, J = 10.5, 2 Hz, 1 H), 5.15 (dd, J = 16.5, 2 Hz, 1 H), 5.82 (d, J = 11.5 Hz, 1 H), 6.13 (dd, J = 15, 10.5 Hz, 1 H), 6.40 (dt, J = 16.5, 10.5 Hz, 1 H), 6.49 (dd, J = 15, 11.5 Hz, 1 H); UV (ϵ) 42 500 (282), 54 000 (275), 38 000 (265); CD $(\Delta\epsilon)$ −3.1 (287 nm), −4.1 (275 nm), −3.7 (263 nm), +1.4 (221 nm). Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.76; H, 11.20.

(*Z*)-5-((*aS*)-4-Methylcyclohexylidene)-1,3-pentadiene (7Z). This was prepared from **2Z** in a manner analogous to the preceding preparation. Triene **7Z** gave $[\alpha]^{25}{}_{546}$ −9.3° (*c* 0.5, cyclohexane); IR (film) 3070 (w), 3020 (w), 2960, 2850, 1685, 1630, 1460, 1010, 920, 755. ^{1}H NMR 0.90 (d, J = 7 Hz, 1 H), 0.85–2.35 (m, 8 H), 2.77 (br d, J = 12 Hz, 1 H), 5.10 (dd, J = 10.5, 2 Hz, 1 H), 5.20 (dd, J = 16.5, 2 Hz, 1 H), 5.92 (m, 1 H), 6.25 (d, J = 5 Hz, 2 H), 6.86 (dt, J = 16.5, 10.5, 10.5 Hz, 1 H); UV (ϵ) 28 400 (286 nm), 38 600 (275 nm), 31 300 (265 nm); CD $(\Delta\epsilon)$ −0.5 (276 nm). Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.74; H, 11.12.

Ethyl (2*E*,4*E*)-6-((*aS*)-4-Methylcyclohexylidene)-2,4-hexadienoate (8E,E) and Ethyl (2*Z*,4*E*)-6-((*aS*)-4-Methylcyclohexylidene)-2,4-hexadienoate (8Z,E). The synthesis was carried out as described for the preparation of **5E** and **5Z** using aldehyde **2E** as starting material. After radial chromatography (hexane–5% diethyl ether) the two isomeric esters were obtained in 37% **8Z,E** and 42% **8E,E** yields.

8Z,E: $[\alpha]^{19}{}_{546}$ −137.5° (*c* 1.0, cyclohexane); IR (film) 3040 (w), 2960, 2850, 1710, 1640 (w), 1610, 1575, 1460, 1200, 1180, 1050, 975; 835; ^{1}H NMR 0.89 (d, J = 7 Hz, 3 H), 0.85–2.35 (m, 8 H), 1.30 (t, J = 7 Hz, 3 H) 2.79 (br d, J = 12 Hz, 1 H), 4.19 (q, J = 7 Hz, 2 H), 5.57 (d, J = 11.5 Hz, 1 H), 5.99 (d, J = 11.5 Hz, 1 H), 6.62 (t, J = 11.5, 11.5 Hz, 1 H), 6.76 (dd, J = 15, 11.5 Hz, 1 H), 7.44 (dd, J = 15, 11.5 Hz, 1 H); UV 39 700 (314 nm); CD $(\Delta\epsilon)$ −5.3 (314 nm), −0.93 (224 nm); MS calcd $C_{15}H_{22}O_2$ 234.1620, found 234.1616.

8E,E: $[\alpha]^{19}{}_{546}$ +32.5° (*c* 1.1, cyclohexane); IR (film) 3020 (w), 2960, 2850, 1710, 1640 (w), 1615, 1585, 1460, 1350–1100, 1060, 1015; ^{1}H NMR 0.91 (d, J = 7 Hz, 3 H), 0.90–2.30 (m, 8 H), 1.30 (t, J = 7 Hz, 3 H), 2.78 (br d, J = 12 Hz, 1 H), 4.20 (q, J = 7 Hz, 2 H), 5.82 (d, J = 15 Hz, 1 H), 5.91 (d, J = 11 Hz, 1 H), 6.22 (dd, J = 15, 11 Hz, 1 H), 6.83 (dd, J = 15, 11 Hz, 1 H), 7.34 (dd, J = 15, 11 Hz, 1 H); UV (ϵ) 49 200 (319 nm), 48 800 (308 nm); CD $(\Delta\epsilon)$ ca. 0 at UV$_{\max}$; MS calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1622.

The **8E,E** ester could also be obtained as the main product of condensation of the aldehyde **20** with the anion of triethyl 4-phosphonocrotonate. The optical purity of the product was, however, significantly diminished.

Ethyl (2*E*,4*Z*)-6-((*aS*)-4-Methylcyclohexylidene)-2,4-hexadienoate (8E,Z) and Ethyl (2*Z*,4*Z*)-6-((*aS*)-4-Methylcyclohexylidene)-2,4-hexadienoate (8Z,Z). The reaction was carried out as for preparation of **8Z,E** and **8E,E** using aldehyde **2Z** as starting material. The two isomeric products were obtained in 26% (**8Z,Z**) and 12% (**8E,Z**) yields.

8Z,Z: $[\alpha]^{25}{}_{546}$ −5.9° (*c* 0.9, cyclohexane); IR (film) 3040 (w), 2960, 2850, 1710, 1630 (w), 1610, 1565 (w), 1460, 1185, 1060, 825; ^{1}H NMR 0.91 (d, J = 7 Hz, 3 H), 0.95–2.35 (m, 8 H), 1.30 (t, J = 7 Hz, 3 H), 2.82 (br d, J = 12 Hz, 1 H), 4.19 (q, J = 7 Hz, 2 H), 5.65 (d, J = 11.5 Hz, 1 H), 6.35 (d, J = 11.5 Hz, 1 H), 6.63 (t, J = 11.5, 11.5 Hz, 1 H), 7.13 (t, J = 11.5, 11.5 Hz, 1 H), 7.17 (t, J = 11.5, 11.5 Hz, 1 H); UV 33 100 (314 nm); CD $(\Delta\epsilon)$ −0.5 (305 nm), −0.2 (221 nm); MS calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1611.

8E,Z: $[\alpha]^{25}{}_{546}$ −15.8° (*c* 0.4, cyclohexane); IR (film) 3030 (w), 2960, 2850, 1710, 1615, 1570 (w), 1460, 1350–950, 890; ^{1}H NMR 0.92 (d, J = 7 Hz, 3 H), 0.95–2.30 (m, 7 H), 1.30 (t, J = 7 Hz, 3 H), 2.34 (br d, J = 12 Hz, 1 H), 2.80 (br d, J = 12 Hz, 1 H), 4.23 (q, J = 7 Hz, 2 H), 5.85 (d, J = 15 Hz, 1 H), 6.00 (t, J = 11.5, 11.5 Hz, 1 H), 6.40 (d, J = 11.5 Hz, 1 H), 6.59 (t, J = 11.5, 11.5 Hz, 1 H), 7.81 (dd, J = 15, 11.5 Hz, 1 H); UV (ϵ) 38 800 (310 nm); CD $(\Delta\epsilon)$ −0.65 (308 nm); MS calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1636.

(*E*)- and (*Z*)-5-((*aS*)-4-Methylcyclohexylidene)-3-penten-2-ones (3E and 3Z). A mixture of the esters **5E** and **5Z** (1.0

g) was saponified at room temperature by stirring overnight with 5 mL of methanol and 5 mL of 2 N NaOH. After standard workup the *Z*/*E* mixture of free acids was obtained in quantitative yield. A sample of the mixture of acids was esterified with diazomethane. GLPC analysis of the esters shows that their ratio was exactly the same (*E*:*Z* 57:43) as the starting material. The mixture of acids (0.72 g, 4 mmol) in anhydrous THF (30 mL) was treated at 0 °C with 10 mL of 1.5 M MeLi. After stirring for 2 h Me_3SiCl (2 mL) was added at once,[26] and the mixture was allowed to warm to room temperature. After addition of 1 N HCl (30 mL), the mixture was extracted with hexane and washed with 2 N NaOH. The organic products (0.66 g) were redissolved in dichloromethane and filtered through silica gel. The two isomeric dienones **3E** and **3Z** were separated by radial chromatography (hexane–10% diethyl ether), yield 30% and 17%, respectively (isomer **3Z** is unstable).

3E: $[\alpha]^{25}_{546}$ +45.4° (*c* 1.0, cyclohexane); IR (film) 3020 (w), 2960, 2850, 1670, 1625, 1585, 1455, 1280, 980, 890; ^1H NMR 0.93 (d, *J* = 7 Hz, 3 H), 0.90–2.45 (m, 8 H), 2.28 (s, 3 H), 2.90 (br d, *J* = 12 Hz, 1 H), 5.97 (d, *J* = 11.5 Hz, 1 H), 6.09 (d, *J* = 15 Hz, 1 H), 7.48 (dd, *J* = 15, 11.5 Hz, 1 H); UV (ε) 150 sh (335 nm), 30 500 (281 nm); CD (Δε) –0.044 (347 nm), +1.2 (287 nm); MS calcd for $C_{12}H_{18}O$ 178.1358, found 178.1353.

3Z: $[\alpha]^{25}_{546}$ –68.1° (*c* 0.91 cyclohexane); IR (film) 3030 (w), 2960, 2850, 1680, 1620, 1570, 1440, 1180; ^1H NMR 0.91 (d, *J* = 7 Hz, 3 H), 0.91–2.3 (m, 7 H), 2.22 (s, 3 H), 2.38 (br d, *J* = 12 Hz, 1 H), 2.87 (br d, *J* = 12 Hz, 1 H), 5.93 (d, *J* = 11.5 Hz, 1 H), 6.77 (t, *J* = 11.5, 11.5 Hz, 1 H), 7.18 (d, *J* = 11.5 Hz, 1 H); UV (ε) 180 sh (340 nm), 19 700 (291 nm); CD (Δε) –1.4 (290 nm); MS calcd for $C_{12}H_{18}O$ 178.1358, found 178.1341.

In addition, small amounts of the hydroxy dienes **18** and **19** were isolated by radial chromatography.

18: ^1H NMR 0.90 (d, *J* = 7 Hz, 3 H), 0.9–2.3 (m, 8 H), 1.34 (s, 6 H), 2.76 (br d, *J* = 12 Hz, 1 H), 5.73 (d, *J* = 15 Hz, 1 H), 5.77 (d, *J* = 11.5 Hz, 1 H), 6.48 (dd, *J* = 15, 11.5 Hz, 1 H); UV (ε) 29 100 (241.5 nm); CD (Δε) –3.0 (241 nm).

19: ^1H NMR 0.90 (d, *J* = 7 Hz, 3 H), 0.91–2.2 (m, 7 H), 1.42 (s, 6 H), 2.28 (br d, *J* = 12 Hz, 1 H), 2.76 (br d, *J* = 12 Hz, 1 H), 5.42 (d, *J* = 11.5 Hz, 1 H), 6.19 (t, *J* = 11.5, 11.5 Hz, 1 H), 6.55 (d, *J* = 11.5 Hz, 1 H); UV ε 23,000 (244 nm); CD Δε–4.1 (241 nm), ;+2.5 (209 nm).

(*E*)-6-((*aS*)-4-Methylcyclohexylidene)-2,2-dimethyl-4-hexen-3-one (4E). A similar procedure to that for preparation of **3E** and **3Z** was carried out with *t*-BuLi in pentane in place of MeLi. After workup and radial chromatography only unstable dienone **4E** could be isolated (16%) in pure form: mp 59–65 °C; $[\alpha]^{25}_{546}$ +57.7° (*c* 1, cyclohexane); IR (film) 3030 (w), 2960, 2850, 1670, 1625, 1585, 1460, 1080; ^1H NMR 0.8–2.4 (m, 8 H), 0.90 (d, *J* = 7 Hz, 3 H), 1.16 (s, 9 H), 2.94 (br d, *J* = 12 Hz, 1 H), 5.99 (d, *J* = 11.5 Hz, 1 H), 6.49 (d, *J* = 15 Hz, 1 H), 7.48 (dd, *J* = 15, 11.5 Hz, 1 H); UV 180 sh (335 nm), 26 100 (287 nm); CD (Δε 0.03 (350 nm), +1.6 (287 nm); MS calcd for $C_{15}H_{24}O$ 220.1827, found 220.1830.

1-((*aS*)-4-Methylcyclohexylidene)-3,3-dimethyl-2-butanone (14). A solution of the aldehyde **20** (415 mg, 3 mmol) in pentane (10 mL) was treated in an ice bath under N_2 with 45 mL of 1.5 M *t*-BuLi in pentane. After 15 min., water was added, the solution was stirred 15 min. and filtered through silica gel, and the isomeric carbinols were eluted with dichloromethane (420 mg). The dichloromethane solution was stirred with 3 g of MgO_2 for 24 h, followed by addition of another portion of MnO_2 (3 g), and stirring was continued for 24 h. The mixture was filtered and the product purified by radial chromatography (hexane–2% diethyl ether) to yield 146 mg (25%) of a low melting solid: $[\alpha]^{24}_{546}$ +65.3° (*c* 1.5, cyclohexane); IR (film) 3020 (w), 2960, 2850, 1680, 1460, 1085, 870; ^1H NMR 0.91 (d, *J* = 7 Hz, 3 H), 0.9–2.3 (m, 8 H), 1.14 (s, 9 H), 3.58 (br d, *J* = 13 Hz, 1 H), 6.21 (s, 1 H); UV (ε) 73 (333 nm), 14 000 (236 nm); CD (Δε) –0.025 (367 nm), +0.069 (326 nm), +2.7 (237 nm). Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found, C, 80.36; H, 11.49.

(*aS*)-(4-Methylcyclohexylidene)acetone (13) was prepared in a manner similar to the preparation of **14**, using MeLi instead of *t*-BuLi: yield 66%; $[\alpha]^{25}_{546}$ +85.3° (*c* 1, cyclohexane); IR (film) 2960, 2850, 1680, 1620, 1460, 1190, 1170, 950; ^1H NMR 0.92 (d, *J* = 7 Hz, 3 H), 0.95–2.25 (m, 8 H), 2.18 (s, 3 H), 3.69 (br d, *J* = 13 Hz, 1 H), 6.00 (s, 1 H); UV (ε) 56 (329 nm), 13 600 (236 nm); CD (Δε) –0.05 (363 nm), +2.9 (235 nm). Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.97; H, 10.64.

Anti and Syn Oximes of (*aS*)-(4-Methylcyclohexylidene)acetaldehyde (21 and 22). Aldehyde **20** (330 mg, 2.4 mmol) in 2 mL of H_2O–MeOH (1:1) was stirred with NH_2OH (210 mg, 3 mmol) while Na_2CO_3 (160 mg, 1.5 mmol) in H_2O (0.5 mL) was added. Stirring was continued for 1 h, MeOH was removed in vacuo, and the products were extracted with diethyl ether. The isomeric oximes **21** and **22** were separated by radial chromatography (hexane–10% diethyl ether) (anti isomer being less polar), with the combined yield of 272 mg (74%) (21:22 ca. 3:2).

Anti/syn assignment was made on the basis of ^1H NMR spectra.

21 (anti): $[\alpha]^{25}_{546}$ +17.2° (*c* 0.8, cyclohexane); IR (film) 3200, 3050, 2960, 2850, 1650, 1460, 1000, 960; ^1H NMR 0.91 (d, *J* = 7 Hz, 3 H), 0.91–2.2 (m, 7 H), 2.31 (br d, *J* = 13 Hz, 1 H), 2.72 (br d, *J* = 13 Hz, 1 H), 5.87 (d, *J* = 10 Hz, 1 H), 8.08 (d, *J* = 10 Hz, 1 H), 9.22 (br s, 1 H); UV (ε) 21 600 (237 nm); CD (Δε) –1.7 (224 nm).

22 (syn): $[\alpha]^{25}_{546}$ –95.9° (*c* 1.0, cyclohexane); IR (film) 3200, 3040, 2960, 2850, 1645, 1460, 940; ^1H NMR 0.92 (d, *J* = 7 Hz, 3 H), 0.95–2.25 (m, 7 H), 2.36 (br d, *J* = 13 Hz, 1 H), 2.80 (br d, *J* = 13 Hz, 1 H), 6.47 (d, *J* = 9 Hz, 1 H), 7.39 (d, *J* = 9 Hz, 1 H), 9.28 (very broad, 1 H); UV (ε) 20 200 (234 nm); CD (Δε) –5.0 (231 nm).

(*aS*)-(4-Methylcyclohexylidene)acetonitrile (9). A mixture of oximes **21** and **22** (2 mmol) in 3 mL of dichloromethane was treated at 0 °C with 0.7 mL (9 mmol) of pyridine and 0.3 mL (2.2 mmol) of trifluoroacetic anhydride.[27] Stirring was continued for 4 h. After addition of water (one drop), the mixture was filtered through silica gel with dichloromethane as eluent. The products were analyzed by TLC to show that anti oxime **21** was mostly unreacted. The nitrile was separated by radial chromatography (hexane–5% diethyl ether): $[\alpha]^{25}_{546}$ +88.8° (*c* 0.6, cyclohexane); IR (film) 3030 (w), 2960, 2850, 2220, 1630, 1460, 810; ^1H NMR 0.92 (d, *J* = 7 Hz, 3 H), 0.95–2.30 (m, 7 H), 2.37 (br d, *J* = 13 Hz, 1 H), 2.90 (br d, *J* = 13 Hz, 3 H), 5.05 (s, 1 H); UV (ε) 15 800 (213.5 nm); CD (Δε) +1.4 (215 nm). Anal. Calcd for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.36. Found: C, 79.95; H, 9.71; N, 10.21.

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Registry No. **2E**, 102633-30-7; **2Z**, 102633-31-8; **3E**, 102633-32-9; **3Z**, 102633-33-0; **4E**, 102633-34-1; **5E**, 102633-35-2; **5Z**, 102633-36-3; **6E**, 102633-37-4; **6Z**, 102633-38-5; **7E**, 102633-39-6; **7Z**, 102633-40-9; **8E,E**, 102633-41-0; **8Z,E**, 102633-42-1; **8E,Z**, 102633-43-2; **8Z,Z**, 102633-44-3; **9**, 102633-45-4; **10**, 102633-46-5; **11**, 28835-97-4; **12**, 77764-44-4; **13**, 102633-47-6; **14**, 102633-48-7; **15**, 102633-49-8; **16**, 102633-50-1; **17**, 102633-51-2; **18**, 102633-52-3; **19**, 102633-53-4; **20**, 102633-54-5; **21**, 102633-55-6; **22**, 102633-56-7; ethyl (trimethylsilyl)acetate, 4071-88-9; diethyl (cyanomethyl)phosphate, 2537-48-6; methyltriphenylphosphonium bromide, 1779-49-3.

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(28) A recent MM2 calculation carried out on ester **12** showed a moderate preference (0.62 kcal/mol) for the cisoid conformation. We thank Prof. A. Padwa for providing us with this data.