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A SYMMETRY RULE FOR CHIRAL OLEFINS

A. I. SCOTT and A. D. WRIXON
Sterling Chemistry Laboratory, Yale University, New Haven, Conn. 06520

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Abstract—It is shown that the sign of the Cotton effect of the principal ($\pi_x \rightarrow \pi_x^*$) transition of chiral olefins near 200 nm predicts the absolute configuration of the molecule through the olefin octant rule. The onset of a second, oppositely signed optically active transition can frequently be observed near 180 nm and is ascribed to $\sigma \rightarrow \pi^*$ or $\pi_x \rightarrow \pi_y^*$ absorption. Overlap of these transitions serves to explain several apparently anomalous effects.

DESPITE the successful correlation of the sign of the Cotton effect of several optically active transitions of dissymmetrically perturbed chromophores with absolute configuration through appropriate rules of symmetry[1–6] it has not proved an easy task to apply such considerations to the isolated ethylenic chromophore.[7] For not only has the region of interest, *viz* 180–210 nm, been inaccessible to many instruments but also the necessary analysis of the singlet–singlet absorption of the ethylene molecule has been sufficiently controversial[8–13] to retard the development of unequivocal assignments of the appropriate transition energies. However, it is now established[13] that the principal electronic absorption of substituted olefins in the region 185–210 nm (ε ca. 10,000) is the $\pi \rightarrow \pi^*$ (N → V) transition and that interference from the Rydberg ($\pi \rightarrow 3s$; N → R) absorption at longer wavelengths can safely be neglected.[11] In order to estimate the factors influencing the rotational strength of the $\pi \rightarrow \pi^*$ band it is convenient to discuss the observed and calculated energies of ethylene and its derivatives prior to the derivation of the symmetry rule.

UV spectra of olefins

The lowest energy transitions of ethylene and its derivatives which must be considered with respect to the observed Cotton effect of chiral olefins near 200 nm are the $\pi \rightarrow \pi^*$ (N → V) and $\pi \rightarrow 3s$ (N → R) singlet excitations which appear at 164 and 174 nm respectively in ethylene. As shown in Table 1 these transitions are progressively

TABLE 1. OBSERVED METHYL-SUBSTITUTED ETHYLENE UV TRANSITIONS[13] (IN NM)

Number of Methyl Groups	$\pi_x \rightarrow \pi_x^*$ (N → V) nm	$\pi \rightarrow 3s$ (N → R) nm
0	164	174
1	174	185
2(1, 1)	186	201
2(1,2 -*cis*)	175	206
2(1, 2-*trans*)	178	204
3	184	216
4	188	230

shifted to longer wavelength with increasing alkyl substitution.[13] A survey of the position of the $\pi \rightarrow \pi^*$ band in relation to the number of alkyl or ring residue substituents displays a trend which can probably be used for diagnosis only in the case of the tetra-substituted chromophore. Such problems and the dangers inherent in the interpretation of mono-olefin spectra have been discussed previously in terms of substitution and environmental effects.[14] In very few of the published UV absorption spectra of olefins has the low energy medium intensity (N → R) band near 220 nm been recorded as more than a shoulder. At much lower wavelength, on the blue side of the $\pi \rightarrow \pi^*$ band, the onset of intense absorption below 180 nm has been ascribed[14d] to the transitions of the corresponding hydrocarbon skeleton. This leaves the rather broad $\pi \rightarrow \pi^*$ absorption as the only source of rotational strength observed between 185 and 210 nm, since the N → R absorption has been demonstrated[11] to be devoid of measurable rotational strength. The onset of a Cotton effect of opposite sign to that of the $\pi \rightarrow \pi^*$ region can often be observed near 185 nm and this may correspond either to a $\sigma \rightarrow \pi^*$ ($1b_{2g} \rightarrow \pi^*$) or $\pi_x \rightarrow \pi_y^*$ ($3p\pi y$) transition. Thus the ORD and CD phenomena observed near 200 nm can safely be attributed to $\pi \rightarrow \pi^*$ absorption and we must now consider the relative merits of the $\pi_x \rightarrow \pi_x^*$ and $\pi_x \rightarrow \pi_y^*$ transitions.

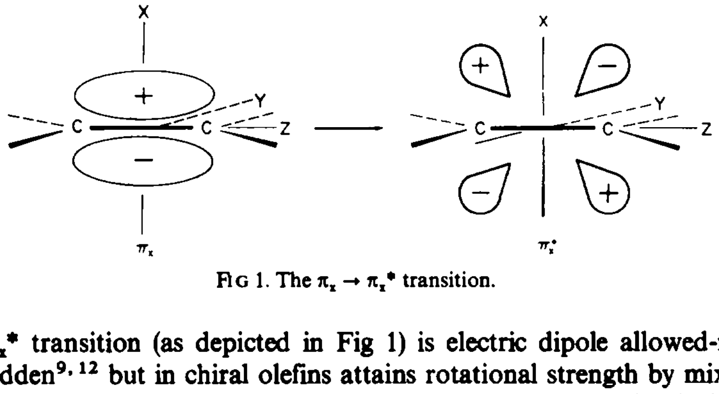


FIG 1. The $\pi_x \rightarrow \pi_x^*$ transition.

The $\pi_x \rightarrow \pi_x^*$ transition (as depicted in Fig 1) is electric dipole allowed-magnetic dipole forbidden[9,12] but in chiral olefins attains rotational strength by mixing with magnetic dipole allowed transitions of the appropriate symmetry under the influences of a perturbing environment.[5] The magnetic dipole allowed transition may correspond to a quadrupole (and magnetic) $\pi_x \rightarrow \pi_y^*$ ($3p\pi y$) band but at present there is insufficient experimental evidence to define the energy orders of the $\sigma \rightarrow \pi^*$ and $\pi_x \rightarrow \pi_y^*$ transitions. Calculations[9,12] however lead us to expect the order shown in Table 2 where band overlapping, especially between $\pi_x \rightarrow \pi_x^*$, $\pi_x \rightarrow \pi_y^*$, and $\sigma \rightarrow \pi^*$ transitions would produce appropriate effects on the ORD-CD curves.

On balance there seems little doubt that the observed CD of monoolefins which appears within a few nm of the N → V absorption and usually at slightly longer

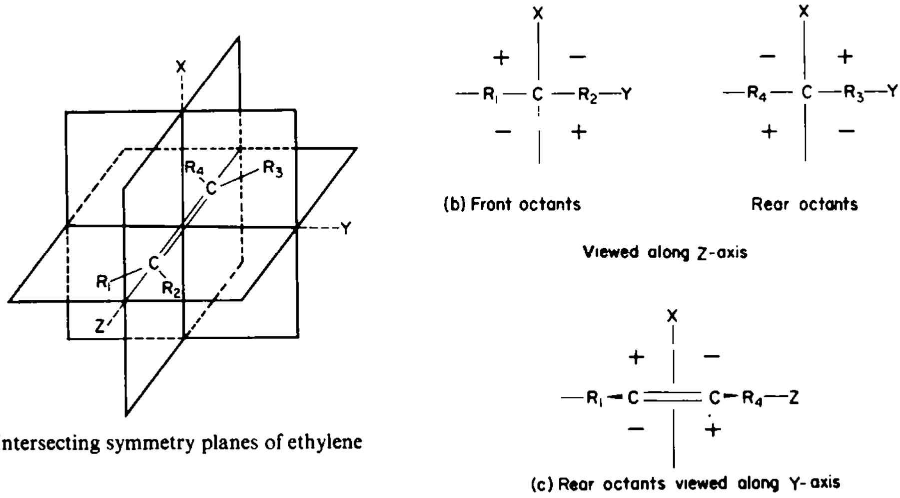
TABLE 2. PREDICTED AND OBSERVED SINGLET TRANSITION ORDER IN ETHYLENE[9,12,13]

	Observed	ε	Predicted
$\sigma \rightarrow \pi_x^*$	?	?	?
$\pi_x \rightarrow \pi_y^*$	7·45 eV	?	8·3 eV
$\pi_x \rightarrow \pi_x^*$	7·6 eV	5,000–10,000	7·8 eV
$\pi \rightarrow 3s$	7·15 eV	500–1,000	7·5 eV

wavelength is $\pi_x \rightarrow \pi_x^*$ which gains rotational strength by mixing with the nearly degenerate $\pi_x \rightarrow \pi_y^*$ or $\sigma \rightarrow \pi^*$ transitions. Recent theoretical work[9, 12] predicts that the $\pi_x \rightarrow \pi_y^*$ band should lie close to the $\pi_x \rightarrow \pi_x^*$ transition, and in this regard it must be noted that $\pi_x \rightarrow \pi_y^*$ has been selected in one study[12] to serve as the main source of rotational strength for *trans*-cyclooctene.

The octant rule

It was pointed out by Schellman[5] that the planar olefin chromophore (point group D_{2h}) under the influence of a dissymmetric static field perturbation should obey a regional octant rule. On the basis of our own[15] and previous CD[11, 16] and ORD[17, 18] measurements we can now show that in fact an octant rule with a left handed coordinate frame (Fig 2) correctly predicts the sign of the 200 nm $\pi \rightarrow \pi^*$ transition. Using the intersecting *xy*, *yz* and *xz* symmetry planes of ethylene (D_{2h}) as octant interfaces (Fig 2), the olefin $R_1R_2C = CR_3R_4$ is viewed in the *z* direction. For those cases where the conformation of the cycloalkene ring is expected to dominate (e.g. cyclohexenes)[19] it is frequently useful to inspect the octants along the *y* axis (Fig 2c). The octant signs of Fig 2 were established by observing the sign of the lowest energy ($\pi \rightarrow \pi^*$) Cotton effect of several olefins of known absolute configuration and comparing this sign with the octant projection of the olefin.



(a) Intersecting symmetry planes of ethylene

(b) Front octants

Rear octants

Viewed along Z-axis

(c) Rear octants viewed along Y-axis

FIG 2. The olefin octant rule.

Owing to the close proximity of the $\pi_x \rightarrow \pi_x^*$, $\pi_x \rightarrow \pi_y^*$ and $\sigma \rightarrow \pi^*$ transitions, the ORD curve of a chiral olefin sometimes consists of a $\pi_x \rightarrow \pi_x^*$ Cotton effect near 200 nm superimposed on a strong background of opposite sign.[17, 18] In fact just such an effect is responsible for the frequent change of sign between $[\alpha]_D$ and the Cotton effect below 200 nm. This effect was adumbrated as long ago as 1935 where the failure of several chiral olefins which showed anomalous dispersion to display an associated electronic absorption was ascribed to the "superposition of two rotations of opposife sign and unequal dispersion in the extreme ultraviolet."[20]

Recently Yogev and Mazur[17, 18] measured the ORD of some steroidal olefins and found that the first (lowest energy) Cotton effect often appears as an inflexion on a

TABLE 3

No.	Compound	Sign of Cotton effect	Predicted sign	CD data [θ]	CD data λnm	ORD data [φ]	ORD data λnm	Refs*
1	5α-Cholest-1-ene	−	−	−9,700 +7,200*	200 190*	−1,620 +13,900*	207 186*	
2	5α-Cholest-2-ene	+	+	+11,900	198	+12,700 0*	205 196*	
3	3-Methyl-5α-cholest-2-ene	+	+	+13,500	200	+12,000 −6,200*	214 190*	
4	11β-,17β-Dihydroxy-17α-methyl-5α-androst-2-ene	+	+	+2,000	198			16
5	5α,25D-Spirost-2-ene	+	+	+14,130	200	+9,510 −3,500*	204 193*	
6	5α-Cholest-3-ene	−	−	−15,600 +45,000*	202 187*	−5,000 +38,900	209 192·5	
7	17β-Hydroxy-5α-androst-3-ene	−	−	−11,600	202			16
8	17β-Acetoxy-5β-androst-3-ene	+	+					18
9	Cholest-4-ene	−	−	−27,600 +27,500*	202 185*	−5,320 +56,000	209 190	
10	17β-Hydroxy-estr-4-ene	+	+					18
11	Cholest-5-ene	+	+	+12,570 −37,700*	202·5 188*			
12	Cholesterol	+	+	+4,900 −19,700*	200 187*			
13	17β-Acetoxy-3,3-ethylene dioxy-androst-5-ene	+	+	+8,600	199			16
14	3,3,17,17-bis ethylene dioxy-11α-hydroxy-androst-5-ene	+	+	+16,500	198			16
15	4,4-Dimethyl-cholest-5-ene	−	−					18
16	17β-Hydroxy-estr-5-ene	−	−					18
17	19-nor-Cholesterol	−	−	−20,000	207			16

* Unless designated by reference number, the data refer to the present work

18	5α-Cholest-6-ene	−	+	−10,290	187	−33,180	205	
						inflection		
						−44,650	197	
						+27,600*	185*	
19	3β-Acetoxy-5α-cholest-6-ene	−	+	−10,000	186	−31,450	205	
						inflection		
						−40,900	195	
						+6,300*	185*	
20	3β,17β-Dihydroxy-5α-androst-6-ene	−	+	−8,250	187			16
21	3β,17β-Diacetoxy-androst-7-ene	−	−					18
22	3β-Hydroxy-ergost-7-ene	−	−	−37,900	210	−21,400	219	
						+31,000	202	
23	3β-Hydroxy-ergost-7,22-diene	−	−	−39,400	210	−21,200	219	
				+5,100*	190*	+35,200	202	
24	Dihydro-lanosterol	+	+	+10,600	205			
				−14,000*	187*			
25	Lanosterol	+	+	+6,600	205			16
26	3β,17β-Dihydroxy-19-nor-androst-5(10)-ene	+	+	+25,000	200			16
27	Androst-9(11)-ene	+	+					18
28	5β-Androst-9(11)-ene	+	+					18
29	3α-Hydroxy-5β-androst-9(11)-ene	+	+	+38,000	204			16
30	3β-Hydroxy-5α,25D-spirost-9(11)-ene	+	+	+31,600	205	+11,900	212	
				−19,400*	190*	−43,400	197	
31	3α-Acetoxy-$\Delta^{9,11}$-5β-norcholenic-acid-methyl ester	+	+	(−2,200	220·5)			
				+43,500	204	+23,000	213	
				−30,100*	190*	−44,800	197	
32	3β-Hydroxy-Δ^{11}-5β-etienic acid methyl ester	−	−	(+11,800	216)	+7,400	233	
				−4,960	202	−9,300	212	
				+20,100	189	+11,900	196	
33	3β-Hydroxy-5α,25D-spirost-11-ene	−	−	−25,600	197·5	−16,500	205	
						+37,500*	190*	
34	3β-Hydroxy-ergost-8(14)-ene	−	−	−25,600	221	−12,000	230	
				+19,300	202	+26,000	212·5	
						−13,400	190	

No.	Compound	Sign of Cotton effect	Predicted sign	CD data		ORD data		Refs
				(θ)	λnm	[φ]	λnm	
35	3β-Acetoxy-ergost-8(14)-ene	–	–	–29,800	221	–13,200	228	
				+26,900	202	+33,100	212·5	
						–11,790*	190*	
36	3β-Acetoxy-$\Delta^{8(14)}$-5β-etienic-acid	–	–	(+3,800	233)	+5,600	240	
	methyl ester			–8,000	221	–410	227	
				+10,000	206	+15,500	214	
						+4,900	201	
37	3β-Hydroxy-ergost-14-ene	–	–	–2,700	210			
38	3β-Acetoxy-Δ^{14}-5β-etienic-acid-	–	–	(+2,200	228)	+580	242	
	methyl ester			–8,000	206	–8,900	215	
						–250	199	
39	3β-Hydroxy-5α-androst-16-ene	–	–	–8,500	195			
40	3α-Hydroxy-5α-androst-16-ene	–	–	–9,200	195			
41	3β,11β-Dihydroxy-20,20-ethylenedioxy-	–	–	–10,900	202	–1,800	212	
	11α-methyl-5α-pregn-16-ene			+10,800*	187*	+22,400	194	
42	3β-Acetoxy-7-methylene-5α-cholestane	+	+	+14,900	196	+1,600	207	
				–21,600*	186*	–29,400*	190*	
43	3β-Acetoxy-11-methylene-5α,25D-	–	–	–10,750	200			
	spirostan			+31,100*	187*			
44	3β-Hydroxy-17-methylene-5α-androstane	+	+	+8,100	195	+12,500	202	
						–13,300*	190*	
45	16β-Methyl-3β,11β,20-triacetoxy-5α	–	–	–43,000	206	–15,200	217	
	pregn-17(20)-ene					+55,000*	190*	
46	3β-Hydroxy-20-methylene-5β-pregnane	+	?	+14,600	202	+7,700	212	
						–11,900	196	
47	3β,11α-Dihydroxy-ergost-22-ene	No detectable CD						
48	3β-Hydroxy-C-nor-D-homo-5α, 25D-	–	?	–40,650	210	–17,400	219	
	spirost-13(17)-ene			+54,500*	187*	+40,300	199	
49	3β-Hydroxy-C-nor-D-homo-5α,25D-	–	–	–14,080	210	–8,700	218	
	spirost-17(18)-ene			+30,600*	188*	+25,400*	190*	
50	Phyllocladene	–	–	+27	223			
				–9,800	203	–3,340	212	
				+24,400*	185*	+13,300*	190*	

51	Iso-phyllocladene	+	+	+41,000	209	+21,030	221	
				−3,800*	190*	−16,180	198	
52	13β-Abiet-7-en-18-oic acid	−	−	(+1,100	227)	−6,800	217	39
				−17,500	207	+14,000*	202*	
53	7-Abieten-18-oic acid	−	−	(+5,700	224)	−13,500	214	39
				−33,000	205	+25,000*	202*	
54	13β-Abiet-8(14)-en-18-oic acid	+	+	+17,000	209	+22,000	217	39
						−10,000*	200*	
55	8(14)-Abieten-18-oic acid	+	+	+37,000	210	+19,500	218	39
						−16,000*	203*	
56	13-Abieten-18-oic acid	−	−	(+2,200	221)	+1,200	227	39
				−4,900	208	−300	215	
						+2,500*	210*	
57	13β-Abiet-8-en-18-oic acid	+	+	+26,500	199	+27,000	210	39
58	8-Abieten-18-oic acid	−	−	−7,300	215	−6,700	225	39
						+6,900*	210*	
59	13(15)-Abieten-18-oic acid	+	?	+5,500	208	+1,350	217	39
60	(+) S 1-isopropylidene-3-methyl cyclopentane	+	+					11
61	(+) R 4-methyl cyclohexene	+	+	+6,000	198	+3,900	207	
						−4,000*	192*	
62	(−) Menth-1-ene	−	−					18
63	(−) Limonene	−	−	−7,750	210	−7,000	217	
				+6,500*	198*	+2,540*	205*	
64	(+) *trans*-Menth-2-ene	−	−					18
65	(+) Sabinene	−	?	−39,200	207	−12,770	219	
				+24,200*	185*	+51,050	195	
66	(−)-β-Pinene	+	?	+50,000	198	+16,430	212	
				−8,850*	185*	−27,000*	185*	
67	(+) α-Pinene	−	?	+4,100	219	+2,100	227	
				−9,000*	190*	−3,800	205	
						−9,000*	195*	
68	(−) R *trans*-cyclooctene	−	−	−140,800	196	−60,900	211	
						+132,000*	185*	

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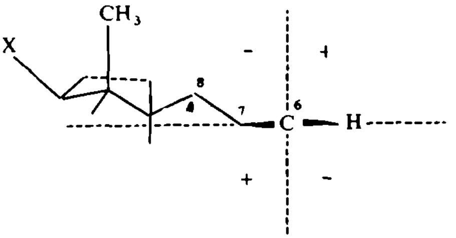
* Lowest recorded values, not a peak or extremum.

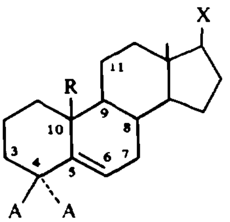
background of opposing sign. The phenomenon is also reflected in the CD curves of several steroidal olefins reported by Legrand and Viennet[16] and ourselves[15] (Table 3).

Typical curves for a number of olefins are shown in Figs 3–12 together with the corresponding octant projection. The second (higher energy) transition of opposite sign is detectable in several cases beginning near 190 nm. Reference to Table 3 reveals that the sign of the Cotton effect near 200 nm is predicted by the octant rule for more than 60 examples. In accord with previous observations[16] it can be seen that the magnitude and sign of the first Cotton effect are approximately constant for a given position and environment of a rigid double bond, most of the CD maxima falling between 197 and 207 nm and red-shifted from the corresponding N → V transition.

Steroids. The examples studied so far included about 50 steroidal olefins (Table 3) covering a full range of isolated double bond positions (Nos 1–41) and including several examples of the exomethylene chromophore (Nos 42–46) side chain (No. 47) and C-nor-D-homo (Nos 48–49) cases. In all of these compounds the sign of the $\pi \rightarrow \pi^*$ Cotton effect could be predicted on the basis of the octant projection obtained by the use of Dreiding models. The presence of allylic methyl groups appears to have a dominating effect upon the Cotton effect sign, whereas the effect of ring residues or alkyl substituents appears to fall off quite markedly with distance. In this regard it will be of considerable interest to carry out accurate vectorial analysis to arrive at rotational strength parameters and hence achieve at least qualitative comparison with the carbonyl octant rule effects. The operation of allylic methyl dominance is well illustrated by the cholest-5-ene series. Thus in 17β-hydroxy estr-5-ene ($R = A = H$; $X = OH$) (No. 16) the octant projection leads to a negative effect determined largely by a population of ring methylene groups. However cholest-5-ene ($R = CH_3$; $A = H$; $X = C_8H_{17}$) (No. 11) has the 19-Me group allylic to the double bond in a positive octant and hence a positive CD is observed ($[\theta] = +12{,}570$ at

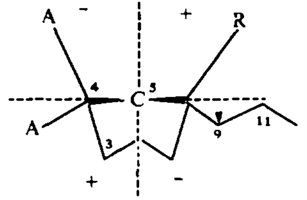


Rear octants, viewed from C_5 to C_6



$X = C_8H_{17}, OH$

$A, R = H, CH_3$



Rear octants, viewed from C_6 to C_5

202 nm). The latter effect is nicely balanced in 4,4-dimethylcholest-5-ene (No. 15) ($R = A = CH_3$; $X = C_8H_{17}$) whose projection leads once again to a predicted and observed negative Cotton effect.

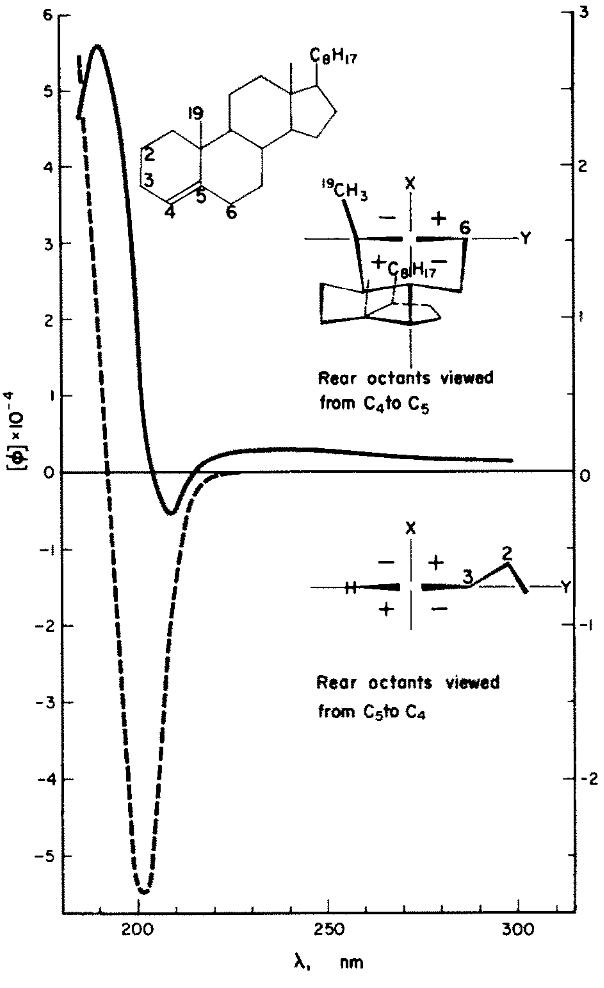


FIG 3. ORD (———) and CD (------) spectra of cholest-4-ene in cyclohexane.

Similarly we observe a sign change between cholest-4-ene (Fig 3; negative) and its 19-nor derivatives (No. 10; positive). The substitution of methyl for hydrogen *on* the double bond has little effect on the rotational strength as can be seen in 3-methyl-5α-cholest-2-ene (No. 3).

Proceeding through the entire series the sole exceptions at first sight appear to be the Δ^6 and $\Delta^{8(14)}$ olefins (*vide infra*). As in the case of conformationally mobile ketones a compound such as No. 46 cannot be safely predicted in the absence of the appropriate low temperature studies.

Diterpenes. Phyllocladene and its isomer (Nos 50, 51) (Figs 4, 5) and the recent series compiled by Burgstahler and Marx[39] (Nos 52–58) are illustrative of diterpenoid olefins. The presence of the carboxylate chromophore whose $n \rightarrow \pi^*$ transition† gives a Cotton effect near 216 nm ($[\theta] \sim 3 \times 10^3$) does not interfere with the intense $\pi \rightarrow \pi^*$ band ($[\theta] \sim 3 \times 10^4$) near 205 nm. 13(15)-Abieten-18-oic acid (No. 59) has sufficient conformational mobility to preclude unambiguous prediction at this time of the observed positive CD.

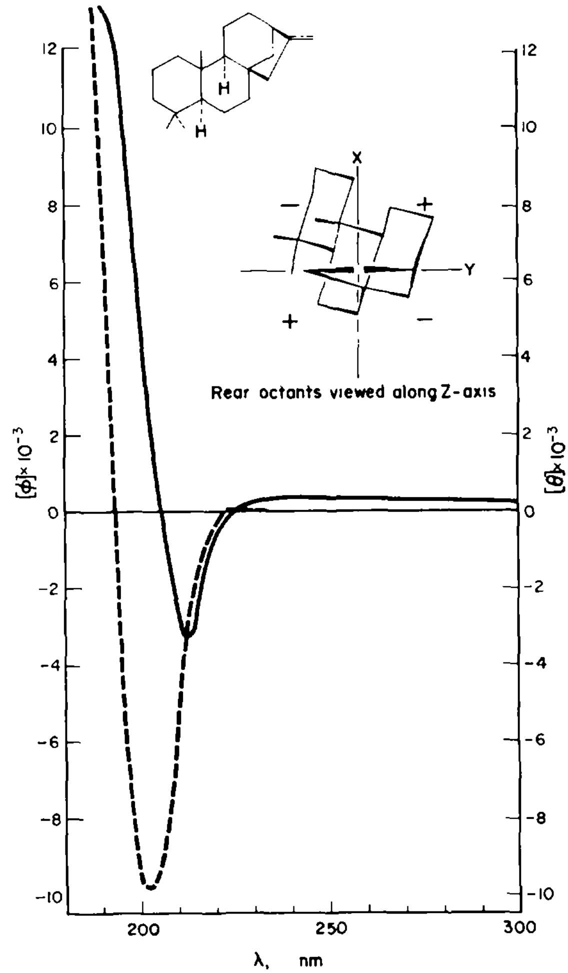


Fig 4. ORD (———) and CD (------) spectra of phyllocladene in cyclohexane.

Monocyclic olefins. Assuming that alkyl substituents on the cycloalkene ring adopt equatorial or pseudo-equatorial positions the Cotton effects of R(+)-4-methylcyclohexene (No. 61) (Fig 6), (−) menth-1-ene (No. 62) and (S) (−) limonene (No. 63) are

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† Indicated in parenthesis in Table 3.

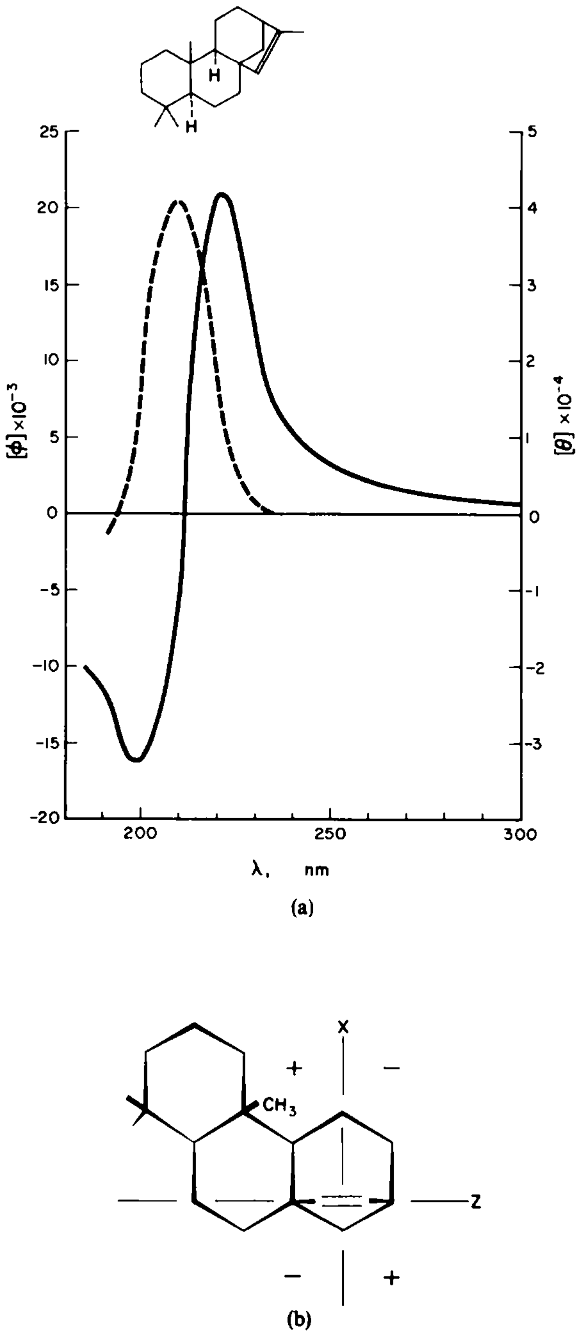

FIG 5. (a) ORD (———) and CD (------) spectra of iso-phyllocladene in cyclohexane; (b) Rear octants viewed along Y-axis.

predicted by the Octant rule. A study of the effects of solvent change and temperature on these compounds is in progress, since the hazards of treating conformationally mobile monocyclic systems are well known. However the CD method may offer a useful probe for conformational analysis of these cases by correlation of the octant population with observed rotational strength.

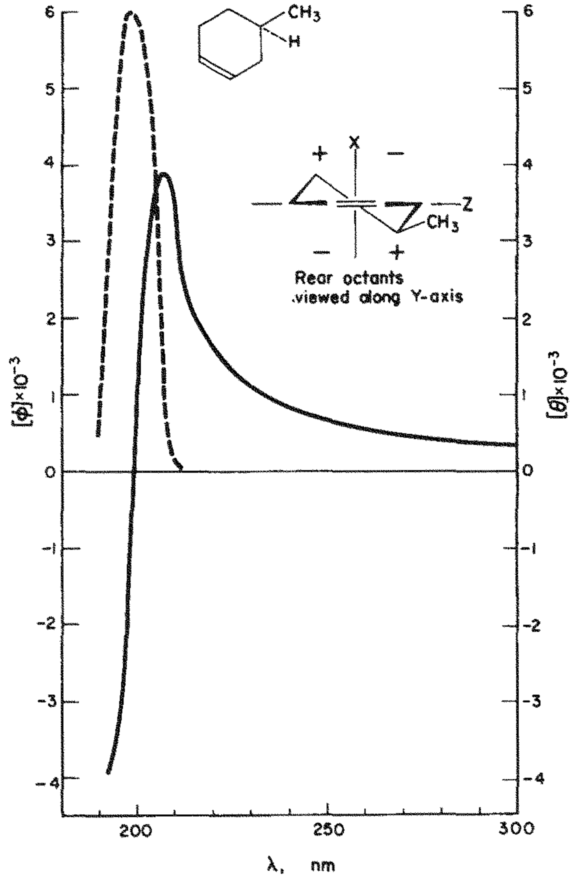

FIG 6. ORD (———) and CD (- - - - - -) spectra of (+) R 4-methyl cyclohexene in cyclohexane.

For the exomethylene cyclopentane (No. 60) studied by Mason and Vane,[11] a C_2[21] conformation with the 3-Me substituent in a pseudo-equatorial position sets the ring carbons 3 and 4 into (dominant) positive octants thus conferring the observed positive Cotton effect.

trans-*Cycloalkenes.* A particularly interesting case of the application of the octant rule concerns the chiral skeleton of *trans*-cyclooctene and its homologues where a merging of the inherently dissymmetric with the "perturbed planar" models might be expected.

Thus the optical activity of *trans*-cyclooctene has long been attributed to the effect of an inherently dissymmetric chromophore and has served as the basis for the theoretical prediction of the sign and magnitude of the rotational strength of twisted ethylene.[9, 12] The fact that in *trans*-cyclooctene (No. 68) the olefin is embedded in an asymmetric environment formed by a "methylene loop" (see Fig 7) has been recognized[22] but the rotatory contributions from such an array have so far been relegated to a subsidiary role in the major calculations on the rotational strengths of olefinic transitions. Now if the symmetry rule is applied directly to *trans*-cyclooctene, assuming for the moment no angle of twist in the ground state, we see from Fig 7 that the octant projection of *trans*-cyclooctene constitutes an example of heavily populated regions of identical sign contributing to the static field perturbation and furthermore that this sign correctly predicts the absolute configuration R^{23} for (−) *trans*-cyclooctene, $[\theta]_{196} = -140{,}800$. If indeed there is severe twist in the ground state this is not reflected in the position (196 nm) of either the CD or UV absorption and although $[\theta]$ is high for a mono-olefin it does appear that the methylene array bears most of

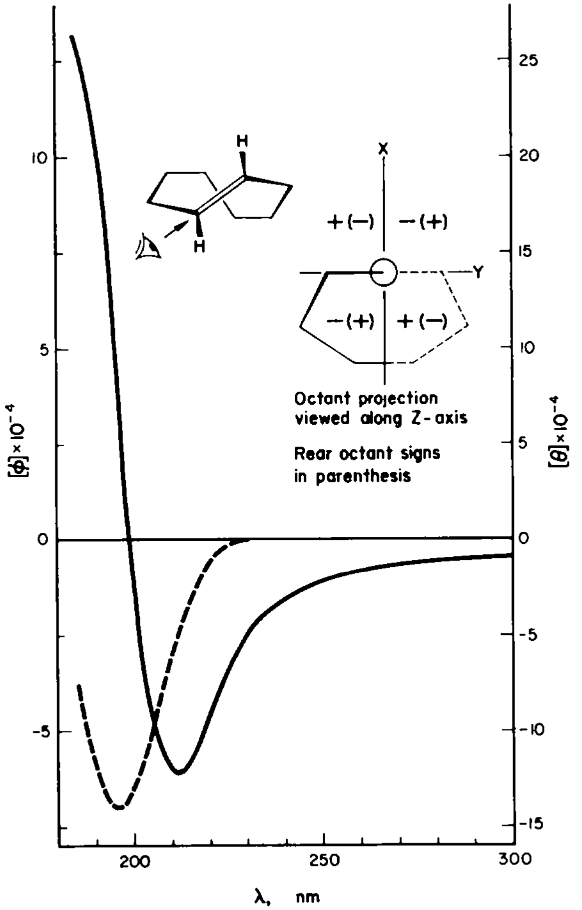

FIG 7. ORD (———) and CD (- - - - -) spectra of (−) R-*trans*-cyclooctene in cyclohexane.

the perturbing influence on the rotational strength of the $\pi_x \rightarrow \pi_x^*$ band of *trans*-cyclooctene. Although dipole moment data suggest[24] a good deal of out-of-plane bending there is no reason to doubt that some degree of twist would allow merging of the asymmetrically perturbed and inherently dissymmetric models for *trans*-cyclooctene itself.[12] This argument cannot be applied to the next homologue, *trans*-cyclononene, for in the case of the nine-membered *trans*-olefin (which racemises readily) it is found[25] that the molecular rotation of a freshly prepared solution ($[M]_D$ ca. 100° $t_{\frac{1}{2}} = 4$ min) is not so far removed from that of cyclooctene ($[M]_D \approx 400°$). We wish to emphasize that the dissymmetric perturbations of twisted *trans*-cyclooctene could still contribute to the rotational strength in an (as yet) undetermined manner. It is still premature to assess the relative position of $\pi_x \rightarrow \pi_x^*$ and $\sigma \rightarrow \pi^*$ or $\pi_x \rightarrow \pi_y^*$ transitions in *trans*-cycloolefins, but it seems that the theoretical model for rotational strength calculations should in fact correspond to the classical one electron theory[26] couched in contemporary terms, and, in turn, to the symmetry correlations summarized by Schellman.[5] We have recently drawn attention[27] to the problems inherent in the relative placing of the transitions of *trans*-cyclooctene as a guide to future models of optical activity for these olefins.

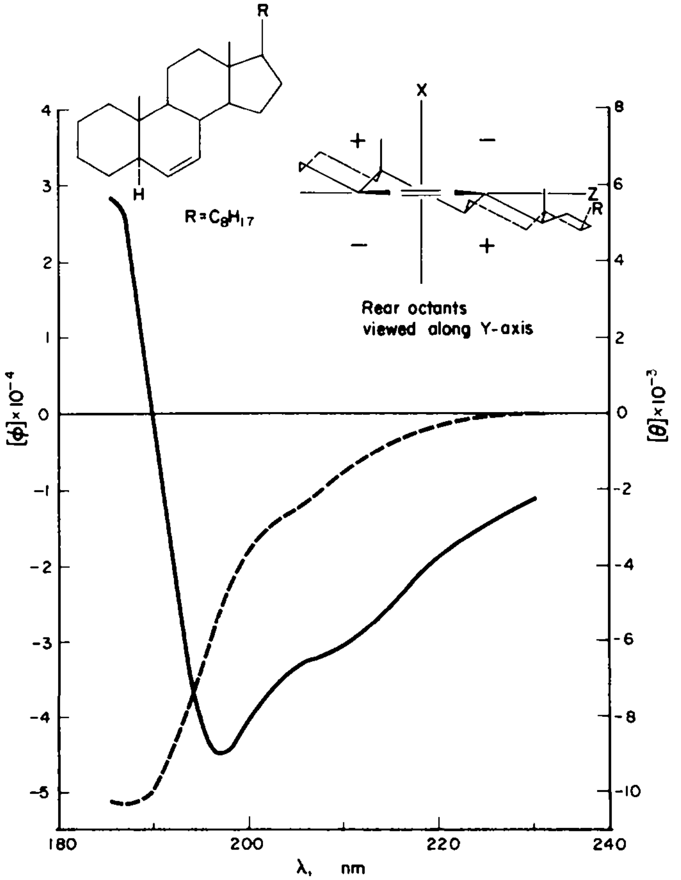

FIG 8. ORD (———) and CD (- - - - - -) spectra of 5α-cholest-6-ene in cyclohexane.

Interpretation of more complex data and apparent exceptions

Δ^6-*Steroids.* Legrand and Viennet[16] found that a pronounced *negative* Cotton effect in 3β, 17β-dihydroxy-5α-androst-6-ene (No. 20) occurred at an exceptionally low wavelength (187 nm) compared with the average value (196 nm) for disubstituted olefins. This seemed remarkable as the UV spectrum is normal and, since octant rule analysis predicts a positive value for the $\pi \rightarrow \pi^*$ transition of the Δ^6-5α-system, we examined two further examples viz 18 and 19. Our measurements confirm the presence of an intense negative Cotton effect near 186 nm but in both the ORD and CD curves of 18 and 19 inflexions occur in the usual $\pi \rightarrow \pi^*$ region. It is apparent from inspection of Fig 8 that the lowest energy *positive* $\pi_x \rightarrow \pi_x^*$ transition at 200 nm is almost completely concealed by the high negative background. This phenomenon which has also been recorded by Mazur[17, 18] may be due to an enhancement of the $\pi_x \rightarrow \pi_y^*$ (or $\sigma \rightarrow \pi^*$) transition caused by the proximity of the octant populations to the *yz* plane. Thus the Δ^6 case is only exceptional in that its $\pi_x \rightarrow \pi_x^*$ band is almost concealed in both CD and ORD by a much more intense transition of opposite sign ($\pi_x \rightarrow \pi_y^*$ or $\sigma \rightarrow \pi^*$) at lower wavelength.†

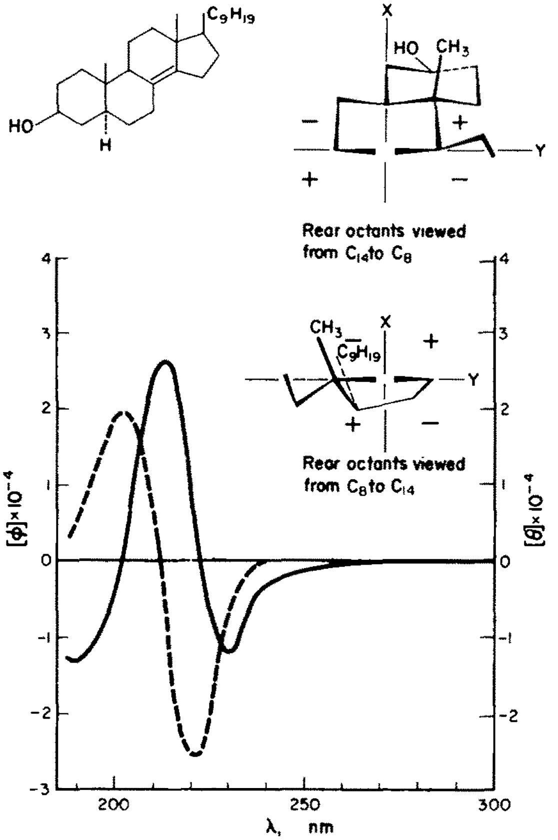

FIG 9. ORD (———) and CD (------) spectra of 3β-hydroxy-ergost-8(14)-ene in cyclohexane.

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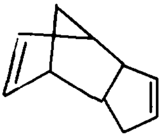
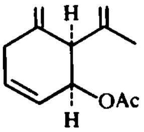
† *Added in proof*: Recent careful measurement of some related Δ^6-olefins has revealed the presence of a positive $\pi_x - \pi_x^*$ CD near 200 nm in support of this idea. A related argument serves to explain the *apparent* exceptions noted recently by Fetizon and Hanna (*Chem. Comm.* 462, 1970).

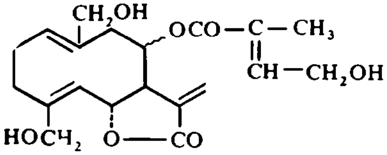
$\Delta^{8,14}$-*Steroids.* An extreme example of the Δ^6 "anomaly" in which not only the relative intensities but also the energies of the two oppositely signed Cotton effects in the 180–210 nm region are so arranged that *two approximately equal and opposite* optically active transitions are concealed under a perfectly normal (λ_{max} 206 nm) electronic absorption band is found in the case of 3β-acetoxy ergost-8(14)-ene (35) and the $\Delta^{8,(14)}$ ester (36). This special situation confers upon both ORD and CD curves (Fig. 9) the *appearance* of exciton splitting.[28] Application of the octant rule to (34), (35) and (36) in which the allylic 18-Me group dominates in a negative octant (Fig. 9) (cf. cholest-4-ene) gives the correct sign (negative) of the lowest energy transition, which, because of the overlap, occurs at 221 nm. The equally intense band of positive sign at 202 nm is then assigned to a red shifted $\pi_x \rightarrow \pi_y^*$ (or $\sigma \rightarrow \pi^*$) transition.



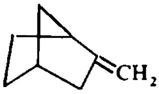
I



II



III



IV

The occurrence of these two almost degenerate transitions with rotational strengths in the opposite sense might cause some confusion in the interpretation of compounds containing non-conjugated diene groups. Under ideal circumstances of inclination and distance the two olefinic groups can act as a coupled oscillator, permitting a given transition to split into two bands of equal and opposite sign. It therefore becomes difficult to distinguish between true exciton splitting[28] and the observation of two oppositely signed olefinic transitions. Perhaps the position might be distinguished by virtue of the splitting approximating to zero near the region of normal $\pi_x \rightarrow \pi_x^*$ maxima. Thus the optical activity of (−) endo dicyclopentadiene[29] (I) could be discussed in this way rather than in terms of the coupled-oscillator theory, since the first CD peak appears normal for a disubstituted olefin. Application of the octant rule to both double bonds of (I) in fact leads to the same absolute stereochemistry (I) as that deduced by assuming the Davydov effect. The same conclusion regarding the stereochemistry of (I) is confirmed through CD studies of the platinum complex.[30]

In a similar manner it now appears possible that the exciton splitting adumbrated[31] in the CD data of carquejyle acetate (II) and its derivatives may have another explanation, since only one intense CD maximum is reported in each case. On the other hand the results for derivatives of jurineolide (III) demonstrate exciton splitting[32] and there is preliminary evidence for the Davydov effect in (+)-(1-R)-5-methylene-bicyclo[2,2,1]hept-2-ene (IV).[33]

"*Reverse*" *effects*

A. *Small rings.* Epoxy and cyclopropyl ketones have been shown to exhibit a reverse octant behaviour[34] for the n → π* ketone transition. However, while the π → π* transition in the cyclopropyl ketone is "normal" the epoxyketone still exhibits reverse octant behaviour for the π → π* band.[35] In this context it is interesting to note that (+) sabinene (Fig 10) [Table 3 (65)] exhibits normal olefin octant behaviour for the $\pi_x \rightarrow \pi_x^*$ Cotton effect. However, the first transition occurs at considerably longer wavelength (205 nm) than is normally observed for disubstituted olefins and this is readily accounted for in terms of conjugation between the olefin and cyclopropane functions, optical exaltation measurements[36] having demonstrated appreciable conjugation in this system.

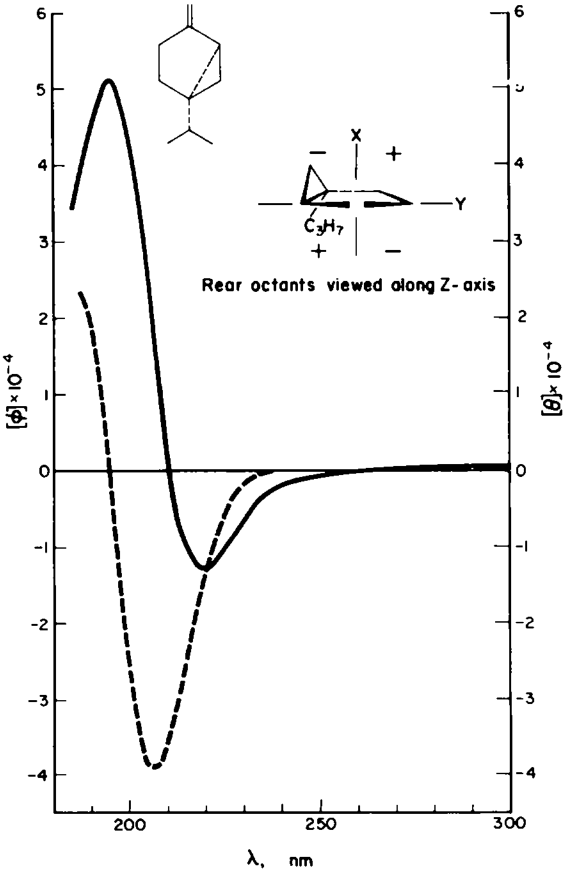


FIG 10. ORD (———) and CD (- - - - -) spectra of (+) sabinene in cyclohexane.

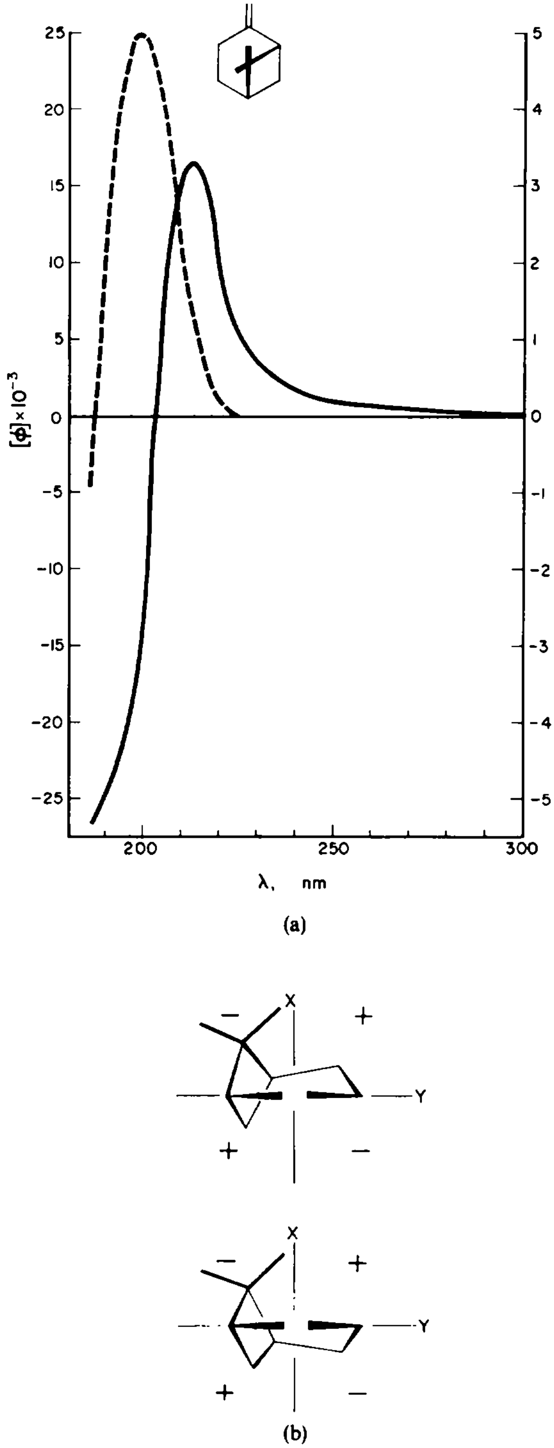


Fig 11. (a) ORD (———) and CD (------) spectra of (−) β-pinene in cyclohexane; (b) Rear octants viewed along z-axis for two possible conformations of (−) β-pinene.

(−) β-Pinene (66) (Fig 11) exhibits an intense positive CD band in a position normal for disubstituted olefins although the octant rule predicts a negative effect. Considerations of this reversal in terms of polarisability make the result less surprising since the cyclobutyl ring is known to possess a low refractivity constant,[37] and hence a "reverse" octant rule may apply here.

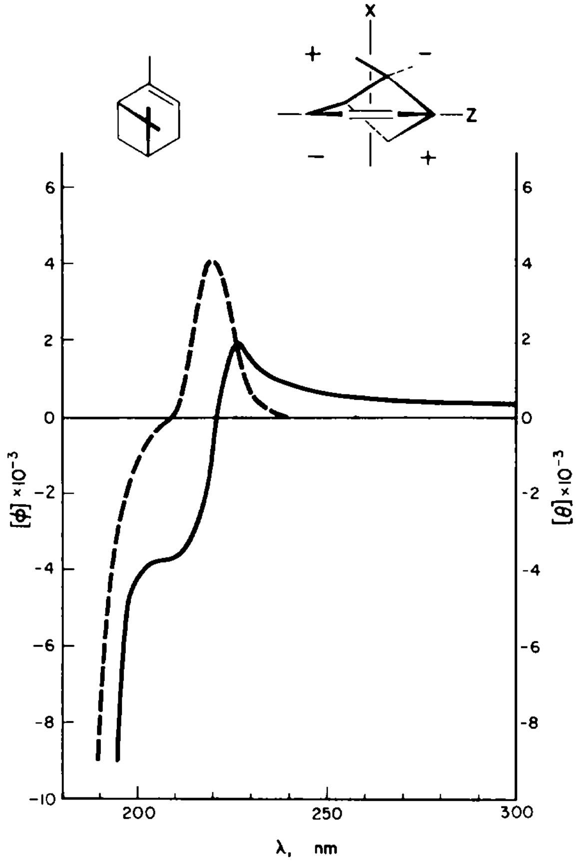


FIG 12. ORD (———) and CD (------) spectra of (+) α-pinene in cyclohexane.

Application of the rule to (+) α-pinene (67) (Fig 12) is also complicated since octants of both signs are occupied. The positive CD maximum occurs at an unusually high wavelength (219 nm). Anomalies have also been noted in the UV spectrum of α-pinene.[13] Further studies on the bicycloolefins are obviously required.

B. *Allylic oxygenated substituents.* Initial results show[30] that hydroxy and methoxy substituents allylic to a double bond exhibit *reverse* octant behaviour. It is probable that the polarisability of the C—OH bond is important in causing this reversal. A more detailed examination of this effect, which, we believe, may form the physical basis for Mills' rule[38] will be discussed in a later paper as part of a fuller treatment of the problems of relative energies and probabilities of $\pi_x \rightarrow \pi_x^*$, $\pi_x \rightarrow \pi_y^*$ and $\sigma \rightarrow \pi^*$ transitions.

In conclusion, it is hoped that on the basis of these empirical correlations a more accurate picture of the transitions of chiral olefins may emerge in theoretical terms and an approach to this problem is now in progress.

EXPERIMENTAL

ORD and CD curves were measured at 25° with a Cary Model 60 spectropolarimeter equipped with a 6001 CD accessory using 10 or 1 mm path length. Sufficient transparency in the low wavelength regions (185–210 nm) was obtained through efficient flushing of the instrument with dry N_2 and use of appropriate concentrations in a 1 mm cell. In all cases measurements were made in cyclohexane soln of spectral grade quality; the CD results recorded earlier by Viennet and Legrand[16] were obtained using solns in EtOH, those of Burgstahler[39] in *n*-hexane.

The data in the Tables are quoted in terms of molecular rotation and molecular ellipticity as previously defined[40] and are given for the extremum or peak maxima except in cases where this could not be reached; then the lowest recorded value is given.

(+) α-Pinene was obtained from Aldrich Chem. Co. and (−) β-pinene and (−) limonene ("purum") from Fluka. The pinenes were purified by vapour phase chromatography on Carbowax 20M (20 ft. column). (−) Limonene was used without further purification.

The steroidal olefins were synthesized by literature methods[cf. 14e] and possessed physical constants in good agreement with those already recorded. 3β-Acetoxy-5α-cholest-6-ene was prepared by the method of Cagliotti[41] but in poor yield, m.p. 104–108°, $[\alpha]_D$ −88° (lit., m.p. 97–105°, $[\alpha]_D$ −88°). Exocyclic methylene derivatives of steroids were formed by Wittig reactions using the procedure of Sondheimer and Mechoulam.[42] *trans*-Cyclooctene was prepared from cyclooctylamine and resolved through its platinum complex with (+) α-methyl benzylamine.[43]

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