

## TETRAHEDRON REPORT NUMBER 22

### AN EMPIRICAL ANALYSIS OF THE CIRCULAR DICHROISM OF CHIRAL OLEFINS†

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**Abstract**—CD data between 185 and 230 nm for 228 chiral olefins have been analysed empirically in order to determine the main features of the relationships between molecular structure and chiroptical properties. Most of the compounds examined are cyclohexene or methylene-cyclohexane derivatives: they include many compounds of steroid type. The regular and generally unstrained structures of such compounds are particularly favourable for initial studies on olefins, as they were earlier for carbonyl compounds. Cyclopentene and methylene-cyclopentane analogues are included for comparison, but are not discussed in detail because of their relatively limited number and less-clearly defined conformations. Olefinic compounds are divided into four classes (A–D), according to their substitution patterns when considered as alkylated ethylene derivatives. In the first stage of the analysis, characteristic wavelengths are recognised for the two (or three) electronic transitions detectable from the CD curves for each class of olefin. Some of the tetrasubstituted-ethylene analogues have optically-active transitions in the regions *ca.* 220 nm and *ca.* 202 nm, but one or other of these transitions may be undetectable from CD curves for some structural types, a feature not appreciated in earlier discussions of olefin CD.

In the second stage of the analysis, the CD curves are studied by the usual empirical method of pairwise comparisons, in order to evaluate the contributions ( $\delta\Delta\epsilon$ ) of structural features to the observed CD at each of the absorption bands. Each of the four substituted-ethylene classes shows its own characteristic behaviour, confirming that no one symmetry rule can be applicable to all chiral olefins.

The main conclusions for the lowest-energy CD band ( $\geq 200$  nm) are:

#### Class A

*1,1-Disubstituted ethylenes.* Exocyclic methylene compounds for the most part follow a carbonyl-like "Octant Rule", the main point of difference being a large consignate ("octant") contribution from a " $\beta$ "-axial methyl group, which can outweigh effects of carbocyclic rings;

#### Class B

*Cis-1,2-disubstituted ethylenes.* Cyclohexene analogues give a CD band with sign corresponding to a consignate effect of allylic axial C–H bonds;

#### Class C

*Trisubstituted ethylenes.* Compounds of the "1-methylcyclohexene" type follow those of class (B) fairly closely, but "trisubstituted ethylene" fragments of the ethylidenecyclohexane type, including " $\Delta^{1(9)}$ -octalin" analogues, give strong CD bands with signs determined by the chirality of the ethylidenecyclohexane unit; an additional feature of " $\Delta^{1(9)}$ -octalin" analogues is a very large dissignate effect accompanying axial alkyl substitution at the allylic carbon atom *trans* to the olefinic C–H bond; alkyl substitution at the other allylic centres has relatively little effect;

#### Class D

*Tetrasubstituted ethylenes.* These compounds generally show rather weak CD curves, but axial-allylic methyl substituents produce dissignate effects.

The CD characteristics associated with the second (higher energy) absorption band ( $< 200$  nm) have also been analysed for each class of olefin, but in less detail because of the lower reliability of data. The sign of this CD band is usually the reverse of that at the lowest energy band, although there are exceptions. The other most noteworthy feature is a significant or even large consignate contribution in some cases when allylic *quasi-equatorial* alkyl substituents are present.

The optical rotatory dispersion and CD of chiral mono-olefins have been discussed in a number of papers since 1965.<sup>2–25</sup> There is little agreement, however, concerning the relationship between structural features and

the shape of the CD curve, and there is still much uncertainty as to the natures of the electronic transitions giving rise to the observed absorption bands. The problem is complicated particularly by the close proximity in energy of several different optically active transitions, resulting in overlap of Cotton effects which is evident in many olefinic CD curves.

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Several different generalisations have been suggested, but no one of them is adequate for all data. The earliest suggestion, from Yogev *et al.* (1967),<sup>7</sup> related the sign of the lowest-energy Cotton effect (ORD) mainly to the chirality contributions of axial allylic C-H bonds (Fig. 1), regarded as an integral part of the chromophore.

Theoretical studies<sup>6</sup> suggested that an Octant Rule is appropriate for olefins, and Scott and Wrixon<sup>10</sup> proposed a "left-handed" Octant-Rule (Fig. 2) on the basis of CD data for 68 olefins of various structural types, many of

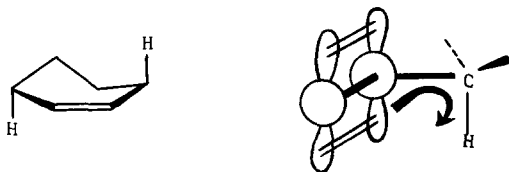
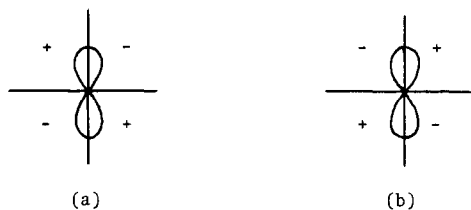


Fig. 1. Positive chirality contribution of quasi-axial allylic C-H bonds in a chiral cyclohexene.



Left-handed Rule (Scott; ref.10) for olefins:

- (a) = front octants
- (b) = rear octants

Right-handed Rule (ref.26) for ketones:

- (a) = rear octants
- (b) = front octants

Fig. 2. Octant Rules; Octant projections as viewed along double-bond axis.

them unsaturated steroids. These authors considered that they were examining the  $\pi_y \rightarrow \pi_x^*$  transition (near 200 nm), with the  $\pi_y \rightarrow \pi_x^*$  and/or  $\sigma \rightarrow \pi_y^*$  transitions lying at slightly higher energy (ca. 180 nm).<sup>†</sup> The simple "left-handed" Octant Rule was soon found to have limited application, however, for Fétizon and Hanna<sup>12</sup> showed that the lowest-energy CD band for most *exo*-methylene steroids appears to obey a "right-handed" Octant Rule, similar to that for the carbonyl  $n \rightarrow \pi^*$  transition (Fig. 3).<sup>26,27</sup> In an attempt to reconcile these observations with the left-handed Octant Rule, the two groups of workers proposed, in a joint paper,<sup>17</sup> that shoulders often seen on the long-wavelength side of the CD band for *exo*-methylene steroids were due to weak overlapping CD bands, always of opposite signs. These weaker bands were therefore regarded as conforming to the "left-handed" rule. Another proposal, by Gawroński and Kielczewski,<sup>15</sup> related the observed CD of methylene steroids mainly to the chirality contribution of homoallylic axial bonds.

The concept of two overlapping CD bands *always* having opposite signs was shown not to have universal

validity when Yogev *et al.*<sup>19</sup> recently reported studies of the linear dichroic absorption of some steroid olefins. This technique enabled them to locate the wavelengths corresponding to the two overlapping absorption maxima of longest wavelength in the UV spectra. By resolution of the composite CD curve they were then able to obtain two CD bands of Gaussian form, having maxima matching the absorption maxima in wavelength. Their results showed that the first two CD curves were often, but not necessarily, of opposite signs. The linear dichroism studies showed, moreover, that the lowest energy transition, here considered to be a Rydberg-like  $\pi \rightarrow 3p_x$  transition, could be polarised in a direction deviating considerably from the C=C bond axis (e.g. in cholest-5-ene); the authors<sup>19</sup> considered that no octant rule based upon elements of molecular symmetry could have general validity for all olefins.

Further developments include elaboration of the allylic axial chirality treatment, and an "Allylic Bond Polarisation" model,<sup>22</sup> which takes account of the sense of polarisation of the allylic axial bonds. Levin and Hoffmann<sup>18</sup> have also considered the possible role of olefin torsion, which appears, from calculations, to be dominant for highly twisted olefins like *trans*-cyclooctene and tricyclo[4.4.0.0<sup>3,8</sup>]dec-4-ene (twistene). (Although unfortunately predicting the wrong sign for the latter compound, which was recently shown to have had its absolute configuration incorrectly assigned in the first instance<sup>28</sup>). The authors<sup>18</sup> suggested that torsional effects should become dominant only for angles of twisting above ca. 10°, larger than would be expected for olefins of essentially unstrained structure, like most unsaturated steroids. Torsional effects have also been discussed by Andersen *et al.*<sup>24</sup>

Drake and Mason<sup>21</sup> assigned a band in the electronic spectrum and CD curves of  $\alpha$ -pinene to the Rydberg  $\pi \rightarrow 3s$  transition; the band is characterised by vibronic structure in the gas-phase CD curve, and a marked blue-shift in solvents of high density. However, this interpretation has recently been questioned.<sup>23</sup>

#### Present work

We have collected and examined CD data for 228 olefinic compounds. Some of these olefins were among those already examined by earlier authors, but we have been able, in many cases, to carry measurements to shorter wavelengths (often 183–185 nm) by the use of hexane as solvent. Many new olefins have been included, some of them synthesised in our own laboratories to provide data for olefinic systems which we judged likely to have particular significance. To widen the scope of our analysis, we have included data published by other workers, where the compounds were not available to us.

With so much uncertainty as to the ordering of transition energies,<sup>10,12,18,19,21,24,29</sup> and varying theoretical guidance as to which transitions would give rise to measurable CD bands, we decided to analyse our data empirically, by seeking regularities with regard to wavelength, sign, and magnitude of observed CD bands, within distinct groups of olefins of related structure. The results of this analysis should prove useful to organic chemists concerned with CD/structure relationships, even though a full theoretical treatment may well lie far in the future. It is, moreover, important that theoreticians should be guided by a reliable set of experimental data for a very large number of compounds, analysed as thoroughly as possible.

<sup>†</sup>The system of coordinates illustrated in Fig. 4 is used throughout this paper (see p. 2479). Other authors have employed different Cartesian systems for olefins.

### Wavelengths of absorption maxima

Although our approach was empirical in that no assumptions were made regarding the nature or ordering of electronic transitions, it was clearly desirable to analyse CD curves into their component bands in a way which would reveal correspondences in wavelength, or small wavelength shifts, within groups of related compounds. Reported UV absorption spectra<sup>30-33</sup> for alkyl-ethylenes show that the lowest-energy absorption band tends to move progressively to longer wavelengths with increasing alkyl substitution. Maxima or pronounced shoulders can often be located at the long-wavelength end of UV curves, in the regions of 198–205 nm for disubstituted ethylenes, 200–216 nm for trisubstituted ethylenes, and 212–230 nm for tetrasubstituted ethylenes. Some recent papers (e.g.<sup>21,29</sup>) assign this last-mentioned band to a Rydberg-type  $\pi \rightarrow 3s$  (or  $\pi \rightarrow 3p_x$ ;  $N \rightarrow R$ ) transition.

Steroidal mono-olefins generally exhibit UV spectra with either maxima or shoulders in the region between 170 and 205 nm, although light-scattering and instrumental difficulties caused discrepancies between several sets of data published between the years 1959 and 1962.<sup>34-38</sup> Disubstituted olefinic bonds (e.g.  $\Delta^1$ ,  $\Delta^2$  or  $\Delta^3$ -steroids) give ill-defined maxima below 192 nm, trisubstituted olefins (e.g.  $\Delta^4$ ,  $\Delta^5$ ,  $\Delta^7$ ,  $\Delta^{9(11)}$ ) give shoulders or maxima between about 190 and 198 nm, whereas tetrasubstituted olefins ( $\Delta^{8(9)}$ ,  $\Delta^{8(14)}$ ) show distinct maxima between 196 and 206 nm. Some variation with solvent has been noted,<sup>35-37</sup> the maxima usually being red-shifted by 1–4 nm in ethanol compared with maxima in a hydrocarbon solvent. The shapes of UV curves are rarely indicative of an isolated absorption maximum, and probably result from overlapping of several transitions. Even those maxima observed may well be displaced from their true wavelengths by the underlying trend of the background absorption curve.

CD curves, especially those which exhibit maxima of opposite signs, provide more reliable indications of the positions of absorption maxima.

Our analysis began with a broad scrutiny of CD data aimed at recognising characteristic wavelengths. For this purpose, olefinic compounds, regarded as ethylene derivatives, were divided into four groups according to ethylene-substitution type, viz

- (A) 1,1-disubstituted (exo-methylene);
- (B) *cis*-1,2-disubstituted (cycloalkene);
- (C) trisubstituted;
- (D) tetrasubstituted.

A fifth group, the *trans*-1,2-disubstituted ethylenes, are represented only by strained *trans*-cycloalkenes,<sup>9,18</sup> which are not included in the present analysis.

CD data for compounds of classes A, B, C and D are collected in Tables 2–5, respectively. Individual compounds are assigned appropriately lettered serial numbers (A1, A2, . . . . ; B1, B2, . . . . , etc.) for ease of reference between the text, and formulae and Tables.

Within each group of olefins we were able to identify a set of characteristic wavelengths which, with small variations according to structural type, could be assigned to the two or three maxima of lowest energy in the composite CD curve.

Some previous authors have used the designations  $\lambda_2$  and  $\lambda_1$  for the wavelengths of the CD band observed at the lowest energy (longest wavelength) and the next CD band of higher energy, respectively. However, we have adopted a reversed order of subscripts, so that observed CD bands are indicated sequentially in order of increasing

energy (decreasing wavelength) by the symbols  $\lambda_1$ ,  $\lambda_2$ ,  $\lambda_3$ , . . . , etc. Unlike the older system, no complications arise when measurements are carried to shorter wavelengths, and third and further CD bands identified.

The present analysis revealed the following regularities:

### Class (A)

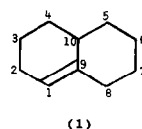
*1,1-Disubstituted ethylenes (exocyclic-methylene compounds)* (Table 2). The wavelength  $\lambda_1$  is generally  $200 \pm 2$  nm for methylene-cyclohexane analogues, and  $\lambda_2$  is probably in the vicinity of 188–190 nm, although less clearly defined. Those few compounds, including 3-methylene-5 $\alpha$ -steroids (A12, 13), which exhibit only a broad CD band with  $\lambda_{\max}$  near 193 nm, do so because two bands of like sign overlap, as has been shown by Yogev *et al.*<sup>19</sup> Each curve of this kind in the present series has been successfully resolved into two Gaussian components (see p. 2479), with maxima in the expected regions. It was not possible to reach a definite conclusion about the few methylene-cyclopentanes listed, but these may conform to the same pattern. Reported UV maxima for exocyclic-methylene steroids lie between 195 and 202.5 nm.<sup>36,37</sup>

### Class (B)

*cis*-1,2-Disubstituted ethylenes (cycloalkenes) (Table 3). Most of the available data refer to cyclohexene analogues, where  $\lambda_1$  is clearly about  $200 \pm 2$  nm in the great majority of cases, but  $\lambda_2$  was often not located as a clearly defined maximum. Most of the compounds in this class showed a very steep CD curve below about 196 nm, with some evidence of a maximum near 185 nm, where the instrument is close to its limiting wavelength. We have tentatively adopted 185 nm as the best estimate available for  $\lambda_2$ . A notable feature in some of the compounds of this group (e.g.  $\Delta^6$ -5 $\alpha$ -steroids; B16–B19) is a tendency for the CD maximum at  $\lambda_1$  to be hidden under the long-wavelength tail of the much stronger curve at  $\lambda_2$ , a point which was noted by earlier workers,<sup>10</sup> and is discussed further on p. 2488. The wavelengths above compare with ill-defined UV maxima variously reported within the range 180–196 nm.<sup>34-38</sup> Cyclopentenes show a single CD maximum near 194 nm, the assignment of which is not clear.

### Class (C)

*Trisubstituted ethylenes* (Table 4). Some of the compounds in this group showed evidence of *three* separate or overlapping CD bands. The first two bands, at  $\lambda_1$  and  $\lambda_2$ , are red-shifted by comparison with disubstituted ethylenes, as a result of the increased substitution of the olefinic bond.<sup>30-34</sup> There is a marked variation, particularly of  $\lambda_1$ , with structural type. Compounds containing the " $\Delta^{10}$ -octalin" moiety (1) in which the double bond is



(1)

exocyclic to one ring, [e.g. oestr-4-enes (C18, 19) and -5-enes (C25–C27), and  $\Delta^7$ -olefinic steroids (C60–C64)] show  $\lambda_1$  at longer wavelengths ( $210 \pm 2$  nm) than do alkyl-substituted cyclohexenes [e.g. 2- or 3-methyl-2-enes (C2, C3) and 3-enes; 202–205 nm]. The Woodward-Fieser-Scott rules<sup>39</sup> for UV absorption of dienes and polyenes include a red-shift of *ca.* 5 nm when the olefinic bond is

exocyclic. Bicyclic structures of the " $\Delta^{1(9)}$ -octalin" type (1) can be regarded as showing a red-shift for the same reason, or because of the presence of two *quasi*-equatorial allylic C-C bonds; those  $\Delta^2$  and  $\Delta^3$ -compounds and their analogues which have *one* such allylic C-C bond [e.g. 3,4 $\alpha$  - dimethyl - 5 $\alpha$  - cholest - 2 - ene; (C4)] also absorb at longer wavelengths than those with no *quasi*-equatorial allylic C-C bonds, although the red-shift is somewhat smaller. We conclude that each *quasi*-equatorial allylic C-C bond increases  $\lambda_1$  by about 2-3 nm. Conversely, a *quasi*-axial allylic C-C bond, typically in 10 $\beta$ -methyl  $\Delta^4$ - and  $\Delta^5$ -steroids, causes a blue-shift of *ca.* 7-10 nm (to 200-202 nm) compared with their 19-nor analogues. Homoallylic polar substituents (e.g. in steroidal 5-enes substituted at C-3) also produce significant shifts in  $\lambda_1$  (p. 2498).

The second CD band ( $\lambda_2$ ) appears usually to lie in the anticipated region between 190 and 195 nm, with the band at  $\lambda_3$  often discernible at lower wavelengths, and in a few cases reaching a maximum near 185 nm. In some cases the CD band at  $\lambda_2$  appears to be missing, and may perhaps be obscured by stronger bands at  $\lambda_1$  and  $\lambda_3$ . UV maxima generally reported<sup>34-38</sup> as lying near 190-195 nm for this class of olefins are presumably those at  $\lambda_2$ , the band at  $\lambda_1$  being a relatively weak UV absorption, though exhibiting strong CD characteristics.

#### Class (D)

*Tetrasubstituted ethylenes* (Table 5). This group of compounds produced the major contrast with earlier findings in the field of olefin CD. Inspection of data in Scott and Wrixon's definitive paper<sup>10</sup> led us to realise that some olefins in this group [e.g. steroidal 8(14)-enes; (D42)-(D45)] gave two CD maxima above 200 nm (*ca.* 221 and 202 nm, respectively), whereas some other compounds, notably the oestr-5(10)-enes (D9)-(D11) showed only one of these CD maxima, near 202 nm. It therefore seemed dangerous to attempt to correlate the CD bands observed at longest wavelength for each of the compounds in this class on the assumption that they were due to the same transition in each case. Instead, we considered the possibility that one transition might be located always near 200 nm, while the longer-wavelength transition might be observable for only some of the compounds in this class,  $\Delta\epsilon$  being essentially zero in other cases which include steroidal 5(10)-enes. Accordingly, we

examined the CD and UV curves of a number of additional tetrasubstituted olefins, including some deliberately synthesized for this purpose. In several cases we observed a very weak Cotton effect ( $\Delta\epsilon \sim 0.3$ ) in the expected region of 220-226 nm, although it was necessary to examine this part of the spectrum for solutions at higher concentration than usual, since concentrations which gave good CD curves near 200 nm failed to reveal the extra CD band above 220 nm.

One such compound was 3-isopropylidene-5 $\alpha$ -cholestane (D1), for which Yogev *et al.*<sup>19</sup> accepted the positive CD band at 209 nm as being the one of lowest energy: our study revealed a further weak CD band ( $\Delta\epsilon + 0.3$ ) at 225 nm. Similar observations are listed in Table 5 for 2,3-dimethyl- $\Delta^2$ -(D6, D7) and a 3,4-dimethyl- $\Delta^3$ -5 $\alpha$ -steroid (D8), where we were able to detect a weak Cotton effect above 220 nm although the first *strong* band was in each case near 198 nm. Since the CD band above 220 nm appears only in compounds of the tetrasubstituted class, and shows abnormal features (see discussion, p. 2504), we designate the wavelength of this band as  $\lambda_0$ . The position of the next CD band (*ca.* 202  $\pm$  8 nm) is designated as  $\lambda_1$ . CD behaviour in the  $\lambda_1$  region shows correspondences with that seen at  $\lambda_1$  for other classes of olefins (p. 2504), and the wavelength corresponds to the first clear maximum observed in the UV spectrum.<sup>34-38</sup> The band at  $\lambda_0$  sometimes appears as a shoulder on the extreme long-wavelength end of the UV absorption curve.

When the tetrasubstituted olefinic bond is in a 5-membered ring, two CD bands appear, at about 210 nm, and 195 nm, respectively. Their assignments are not certain, but we tabulate the bands tentatively as  $\lambda_0$  and  $\lambda_1$ . In some compounds of the tetrasubstituted class, the CD band at  $\lambda_2$  is detectable between 185 and 195 nm, although there are few examples at present where this band has been clearly revealed.

Table 1 summarizes the main conclusions regarding wavelengths of CD bands for the different classes of olefins.

#### Analysis of CD data

The recognition of a regular pattern of wavelengths for CD maxima for each of the four classes of olefins opened the way for an empirical analysis of CD data. Each of the four sets of data was sub-divided so that compounds

Table 1. Characteristic wavelengths of CD maxima for olefins

Olefin Class	$\lambda_0$ (nm) <sup>a</sup>	$\lambda_1$ (nm)	$\lambda_2$ (nm)
(A) 1,1-Disubstituted ethylenes (exocyclic methylene)	-	200 $\pm$ 2	189 $\pm$ 1
(B) 1,2-Disubstituted ethylenes (cyclohexenes)	-	200 $\pm$ 2	<i>ca.</i> 185
(C) Trisubstituted ethylenes (methyl-cyclohexene)	-	203.5 $\pm$ 1.5	192 $\pm$ 3
( $\Delta^{1(9)}$ -octalin)	-	210 $\pm$ 2	192 $\pm$ 3
Increment for alkyl substituent:-			
' $\alpha$ '-quasi-equatorial	-	+2 to +3	?
' $\alpha$ '-quasi-axial	-	-7 to -10	?
(D) Tetrasubstituted ethylenes	215-225	195-210	<i>ca.</i> 185-195

<sup>a</sup> See text, this page and p. 2504.

sharing common structural features within each olefin class could be compared (Tables 2–5). The assumption that contributions ( $\delta\Delta\epsilon$ ) of suitably chosen structural features to the total value of  $\Delta\epsilon$  should be additive has proved to be generally valid in the analysis of CD data for ketones,<sup>1,27</sup> and was adopted in the present work. Group increments derived by pairwise comparisons of related compounds turned out to be rather less consistent than for ketones, but nevertheless permitted empirical “calculations” of  $\Delta\epsilon$  which in most cases gave values of the correct order of magnitude; in only a few cases, usually with special features, were the signs of “calculated”  $\Delta\epsilon$  values wrong.

The results of this inspection of data are summarised in the following sections. The ordering and grouping of compounds in Tables 2–5 has been chosen, as far as possible, to make clear the comparisons which were used in deriving group contributions; discussion is therefore limited largely to the conclusions, their generality, and any special exceptions.

#### Resolution of curves

Where experimental curves were clearly of composite character, with maxima at unusual wavelengths, and with non-Gaussian profile, they were resolved into the Gaussian components which seemed to give the best fit with the experimental curve. Resolutions were carried out

with the aid of a Du Pont 301 Curve Resolver. Figure 3 illustrates typical resolutions. In most cases the separated component curves had maxima near the expected wavelengths: for a few compounds where an equally good fit with the experimental curve could be obtained by summation of two or more different sets of component curves, that set was chosen which exhibited maxima closest to the expected wavelengths. The uncertainties in  $\Delta\epsilon$  values resulting from this procedure were generally rather small (at most 15–20% of observed  $\Delta\epsilon$  values).

**Terminology.** The new terms “consignate” and “dissignate”<sup>40</sup> are used in the following discussion. The mid-point of the olefinic bond is placed at the origin of a frame of right-handed Cartesian coordinates (Fig. 4a), having the  $z$  axis collinear with the olefinic C=C axis, and the  $y$  direction parallel with the axes of the  $p$ -orbitals on the carbon atoms. Unlike the CO group ( $C_{2v}$ ), with only two orthogonal planes of symmetry, ethylene ( $D_{2h}$ ) has three such planes. The fundamental sector rule for olefins must therefore be an “Octant Rule”, although the destruction of elements of symmetry by substituents invalidates a simple “Octant” treatment for chiral olefinic compounds.<sup>19</sup> Nevertheless it is convenient to discuss the locations of substituents in terms of the geometrically-defined octants which they occupy. Most olefinic compounds contain substituents at both “ends” of the double bond. Rather than attempting to visualise “front” and

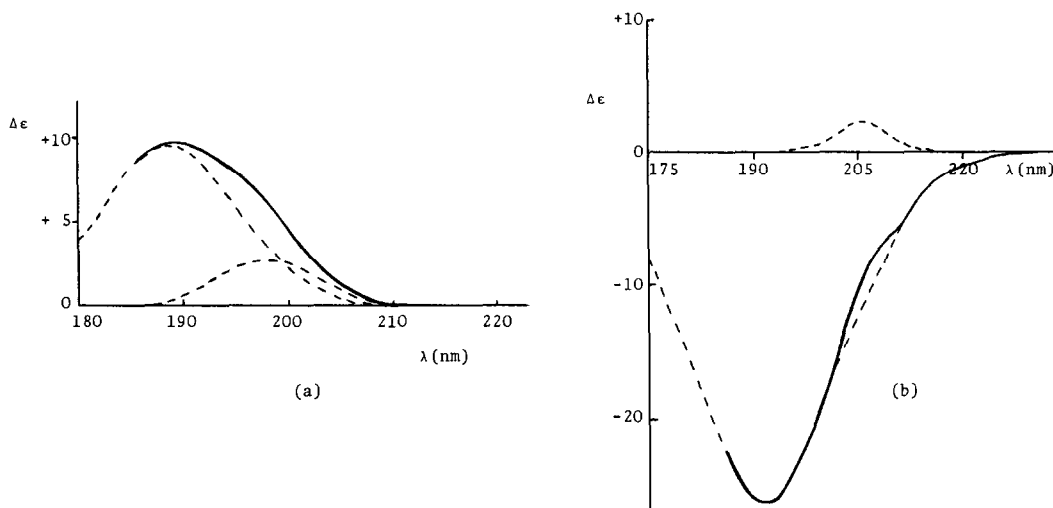


Fig. 3. Use of Du Pont curve resolver for CD curves: (a) 3'-methylene-2 $\alpha$ ,3 $\beta$ -tetramethylene-5 $\alpha$ -cholestane (A14); (b) 5 $\alpha$ -cholest-6-en-3 $\alpha$ -ol (B18); — Experimental curve (instrumental “noise” omitted); ---- resolved component curves.

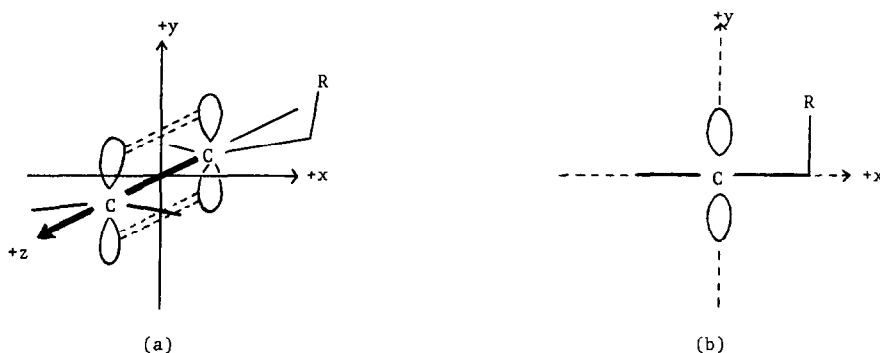


Fig. 4. (a) Coordinate frame for olefins: R is any “axial-allylic” substituent. (b) Projection of “rear” octants (in the  $-z$  direction, as viewed from the origin) showing the position of R in the upper-right octant.

"rear" octants, we consider separately the views of the two "ends" of the double bond as seen from its mid-point, the origin of coordinates (e.g. as in Fig. 4b). "Consignate" behaviour of a substituent at either end of the double bond then coincides with behaviour according to the familiar carbonyl  $n \rightarrow \pi^*$  Octant Rule.<sup>26,27</sup> The term "dissignate" implies that  $\Delta\epsilon$  has the opposite sign,

following the "left handed" octant rule proposed by Scott and Wrixon.<sup>10</sup>

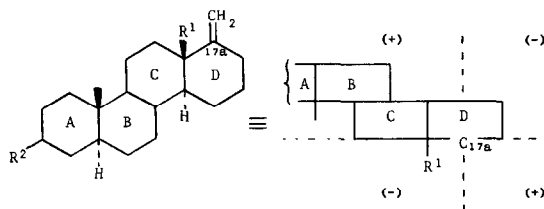
### Class A

1,1-Disubstituted ethylenes (Table 2). Most of the available compounds of this class are of the exomethylene-cyclohexane type, and fall into three sub-

Formulae of Compounds (see Table 2 for names and CD data).

Octant diagrams give the view from the mid-point of the C=C bond.

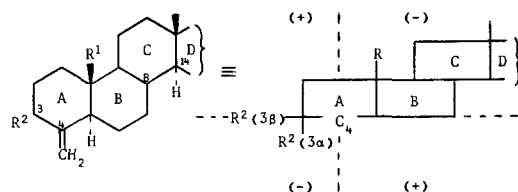
Signs indicated for octants are those which would correspond to *consignate* behaviour (right-handed "Octant Rule").



(A1) Bicyclic, as rings C+D only:  $R^1=H$

(A4)  $R^1=Me$ ,  $R^2=H$

(A5)  $R^1=Me$ ,  $R^2=OAc$



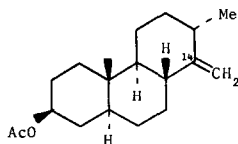
(A2)  $R^1=R^2=H$  (oestrane series)

(A3)  $R^1=Me$ ,  $R^2=H$  (androstane series)

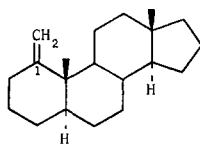
(A6)  $R^1=Me$ ,  $R^2= \alpha\text{-Me}$  (cholestane series)

(A7)  $R^1=Me$ ,  $R^2= \alpha\text{-Me}$  (lupane series,  $8\beta, 14\alpha\text{-Me}_2, 13\beta\text{-H}$ )

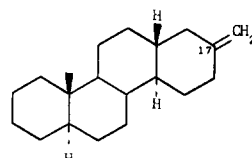
(A8)  $R^1=Me$ ,  $R^2= \beta\text{-Me}$  (cholestane series)



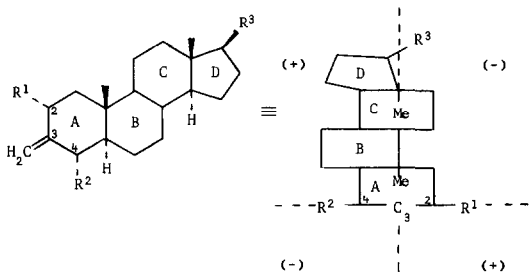
(A9) (octant diagram resembles A2,  $R^1=H$ ,  $R^2= \beta\text{-Me}$ )



(A10)



(A11) (octant diagram quasi-enantiomeric with A12)

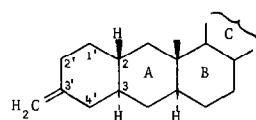


(A12)  $R^1=R^2=R^3=H$

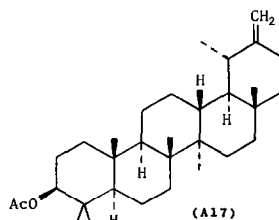
(A13)  $R^1=R^2=H$ ,  $R^3=C_6H_{17}$

(A15)  $R^1=Me$ ,  $R^2=H$ ,  $R^3=OAc$

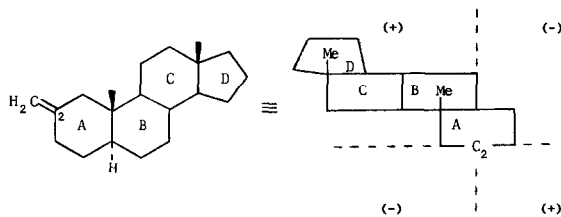
(A16)  $R^1=H$ ,  $R^2=Me$ ,  $R^3=C_6H_{17}$



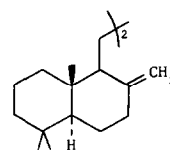
(A14) (octant diagram has some resemblance to A12)



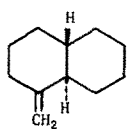
(A17)



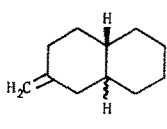
(A18)



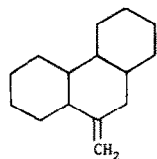
(A19)



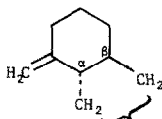
(2)



(3)



(4)



(5)

groups as extended derivatives, respectively, of 1-methylene-*trans*-decalin (2), 2-methylene-*trans* or *cis*-decalins (3), and 9-methyleneperhydrophenanthrene (4);

the last-named compounds, as "middle ring" derivatives, combine the features of both classes of methylene-decalins.

### Group 1

1-Methylene-*trans*-decalins (2). The parent compound (A1) was available from a Wittig reaction<sup>41</sup> with (-)-*trans*-1-decalone.<sup>42</sup> Its absolute configuration is of enantiomeric type to that of 4-methylene-5 $\alpha$ -steroids. The CD contribution at  $\lambda_1$ , attributable to the second ring, is consignate (2 units), while the third ring in 4-methylene-5 $\alpha$ -oestrane (A2), and the 10 $\beta$ -Me group (" $\beta$ "-axial) in the corresponding androstane (A3) add further significant consignate contributions of about 2 and 3-6 units, respectively. Surprisingly, however, the " $\alpha$ "-axial 13 $\beta$ -Me substituent in the (quasi-enantiomeric) 17 $a$ -methylene-D-homo compounds (A4 and A5) makes only a very small consignate contribution (0-2 units).

The most dramatic effect seen in this group of

Table 2. CD data for 1,1-disubstituted ethylenes (exocyclic-methylene compounds)

No.	Compound	SOLVENT: Methanol			Hexane (or cyclohexane)			"Calculated" <sup>b</sup> $\Delta\epsilon$ at $\lambda_1$	Source of compounds <sup>c</sup>	
		C. d. ref. <sup>a</sup>	$\Delta\epsilon$	$\lambda$ (nm)	$\lambda_1$	$\Delta\epsilon$	$\lambda_2$ <sup>d</sup> $\lambda$ (nm)			
<u>1-Methylene-<i>trans</i>-decalin types</u>										
A1	(9 <i>S</i> ,10 <i>R</i> )-1-Methylene- <i>trans</i> -decalin	W			+ 2.0	196	-	-	+2	DNK
A2	4-Methylene-5 $\alpha$ -oestrane	W			- 4.1	199	+6.8!	185!	-4	DNK
A3	4-Methylene-5 $\alpha$ -androstane	{W F}			- 7.2 -10.5	200 200	+4.8! -	187! -	-9	TGH
A4	17 $a$ -Methylene-D-homo-5 $\alpha$ -androstan-3 $\beta$ -ol	W			+ 3.9	196	-7.4!	185!	+4	RJM
A5	17 $a$ -Methylene-D-homo-5 $\alpha$ -androstan-3 $\beta$ -ol, 3-acetate	W			+ 5.9	197	-7.1!	185!	+4	RJM
A6	3 $\alpha$ -Methyl-4-methylene-5 $\alpha$ -cholestane	W			+ 3.6	196	-4.6!	185!	+3	JL
A7	3 $\alpha$ -Methyl-4-methylene compound in Lupane series	W			+ 3.6	199	-7.0!	185!	+3	TGH
A8	3 $\beta$ -Methyl-4-methylene-5 $\alpha$ -cholestane	W			- 3.1	199	+1.0!	187!	-9	JL
A9	14-Methylene-des-D-5 $\alpha$ ,13 $\beta$ (H)-androstan-3 $\beta$ -ol, 3-acetate	W			- 6.0	195	0.0!	185!	-4	DNK <sup>e</sup>
A10	1-Methylene-5 $\alpha$ -androstane	F			- 2.2	199	-	-	-2	
<u>2-Methylene decalin types</u>										
A11	17-Methylene-D-homo-18-nor-5 $\alpha$ -androstane	F			- 5.2	192	(unresolved)		-3	
A12	3-Methylene-5 $\alpha$ -androstane	F			+ 6.4	193	(unresolved)		+3	
A13	3-Methylene-5 $\alpha$ -cholestane	W			+ 6.9 [+ 3.5	195 200	+5.4	190] <sup>f</sup>	+3	DNK
A14	3'-Methylene-2 $\alpha$ ,3 $\beta$ -tetramethylene-5 $\alpha$ -cholestane	W			+ 9.6 [+ 2.7	193 198	+9.5	188] <sup>f</sup>	+3	DNK
A15	2 $\alpha$ -Methyl-3-methylene-5 $\alpha$ -androstan-17 $\beta$ -ol, 17-acetate	W			+10.3 [+ 2.7	190 201	+9.3	191] <sup>f</sup>	+3	DNK
A16	4 $\alpha$ -Methyl-3-methylene-5 $\alpha$ -cholestane	W			+ 2.3	198	0!	185!	+3	TGH
A17	3 $\beta$ -Acetoxy-18 $\alpha$ -urs-20(30)-ene (taraxasteryl acetate)	W	+ 2.3m	203	+ 2.5m	198	-	-	+3	TGH
A18	2-Methylene-5 $\alpha$ -androstane	F			+10.5	197	-	-	+10	
A19	Deoxy-onocerin	W			-14.5	202	-	-	-16	DHRB
A20	3-Methylene-5 $\beta$ -androstane	F			- 3	199	-5.1m	193	-3	
A21	3-Methylene-5 $\beta$ -cholestan-6 $\beta$ -ol, 6-acetate	W			- 4.0	199	ca.0!	186!	-3	DNK
<u>"Middle ring" methylene compounds</u>										
A22	6-Methylene-5 $\alpha$ -oestrane	W			- 0.3	205	-1.0m	185	-3	DNK
A23	6-Methylene-5 $\alpha$ -androstane	F			+ 4.2	197	-	-	+2	

Table 2. (Contd.)

No.	Compound	SOLVENT: Methanol			Hexane (or cyclohexane)			"Calculated" <sup>b</sup> Δε at λ <sub>1</sub>	Source of compounds <sup>c</sup>		
		C.d. ref. <sup>a</sup>	Δε	λ (nm)	λ <sub>1</sub> λ (nm)	Δε	λ <sub>2</sub> <sup>d</sup> λ (nm)				
A24	6-Methylene-5α-cholestane	W			+ 6.3sh 201 [+ 5.6 200]	+6.5m +4.0	193 191] <sup>f</sup>	+2	JH		
A25	6-Methylene-5α-cholestan-3β-ol	W	+ 2.4m	203	+ 3.3 [+ 3.3 196]		196 186] <sup>f</sup>	+2	JH		
A26	6-Methylene-5β,25R-spirostan-3β-ol	W	+ 8.0!	200	+ 9.0		198	+12	DNK		
A27	" " " 3-acetate	W	+ 6.4	202	+ 7.2		199	+12	DNK		
A28	7-Methylene-5α-cholestane	W			- 1sh ca.200 [-0.8±0.2 ca.200]	- 7.5! ca.- 7.5!	185! 185!] <sup>f</sup>	- 1	DNK		
A29	7-Methylene-5α-cholestan-3β-ol	W			1.5		196	- 3.4!	186!	- 1	DNK
A30	" " " 3-acetate	{S {W			+ 4.5 + 3.3		196 195	- 6.6! - 5.5!	186! 196!	- 1	DNK
A31	7-Methylene-des-D-5α,13β(H) androstane	W			- 0.6sh		200	- 3.6	192	- 1	DNK
A32	3,3-Dimethoxy-11-methylene-5α-androstan-17β-ol	W	- 2.7!	202!	- 1.9m		202	+10.5!	190!	?	DNK
A33	17β-Hydroxy-11-methylene-5α-androstan-3-one, 17-propionate	W	-11.4!	197!	- 1.9		200	+ 6.6!	193	?	DNK
A34	" " " 3,3-dimethoxy derivative	W	- 2.5!	204!	- 4.8m		199	+ 2.9!	183	?	DNK
A35	11-Methylene-5α,25R-spirostan	W	- 2.2	203	- 3.4m		202	+11.2!	184	?	JE
A36	11-Methylene-5α,25R-spirostan 3β-ol	W	- 2.3m	205	- 3.5		202	+ 3.2!	194!	?	JE
A37	" " " 3-acetate	{W {S			- 4.0 - 3.3		200 200	+ 6.3! + 9.4!	187! 187!	?	JE
A38	12-Methylene-5α,25R-spirostan	W	+ 3.2!	198!	+ 3.9m		198	-	-	+ 3	JH
A39	" " " 3β-acetoxy derivative Methylene-cyclopentanes	W	+ 3.8!	197!	+ 4.6 [+ 2.5		190 201	+ 7.0!	185!] <sup>f</sup>	+ 3	JH
A40	2-Methylene-A-nor-5α-androstane	F			+ 3.8		202	-	-	(+)	
A41	16-Methylene-5α-androstane	F			- 7.9		193	-	-	(-)	
A42	17-Methylene-5α-androstane	{F {F & S {W			+ 3.8 + 4.9 + 2.7		193 193 194	- - -	- - -	(+)	DNK
A43	17-Methylene-5α-androstan-3β-ol	S			+ 2.5		195	-	-	(+)	
Miscellaneous											
A44	17a-Methylene-C-nor-D-homo-18-nor-13α-spirostan derivative	{W {S	- 3.0m	208	- 3.3m - 4.3		208 210	+4.6! +9.3!	190! 188!	?	DNK
A45	Kaur-16-ene (Phyllocladene)	S			- 3.0		203	+7.4!	185!	?	
A46	Prezizaene	A			+ 5.6		193	-	-	?	
A47	20-Methylene-5α-pregnane	F			+ 1.8		201	-2.4	190	(+)	
A48	20-Methylene-5β-pregnan-3β-ol	S			+ 4.4		202	-	-	(+)	

<sup>a</sup>(See also Tables 3-5) W, Westfield College data; F, Fétizon, ref.12; S, Scott, ref.10; F & S, Fétizon and Scott, ref.17; A, Andersen, ref.43; S(IX), Scott, ref.16; L, Legrand, ref.5; R & D, Rossi and Diversi, ref.14.

<sup>b</sup>Δε calculated from data in Figure 5. (+) or (-) indicates expected sign where no calculated value is available.

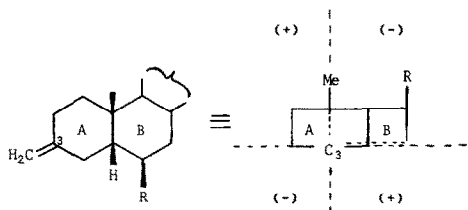
<sup>c</sup>Sources of compounds (see also Tables 3-5).- DHRB: Sir Derek H.R. Barton, F.R.S., London; EAB: E.A. Brown, G.D. Searle and Co., Chicago; SD: Sukh Dev, National Chemical Laboratory, Poona, India; JE: J. Elks, Glaxo Research Ltd., Greenford, Middx.; FF & AT: F. Fringuelli, A. Taticchi, F. Fernandez, D.N. Kirk, and P.M. Scopes, J.C.S. Perkin I, 1974, 1103; TGH: T.G. Halsall, Oxford; JSEH: J.S.E. Holker, Liverpool; LJG: L.J. Gough, Borough Polytechnic, London; JH: J. Hudec, Southampton; HPdeJ: H.P. de Jongh, Organon Laboratories, The Netherlands; DNK: D.N. Kirk, London; MK: M. Kojima, Fukuoka, Japan; DRAL: D.N. Kirk and D.R.A. Leonard, J.C.S. Perkin I, 1973, 1836; JL: J. Levisalles, Paris; BAM: B.A. Marples, Loughborough; JFMG: J.F. McGhie, Chelsea College, London; RJM: D.N. Kirk and R.J. Mullins, J.C.S. Perkin I, 1974, 14; IS: I. Scheer, Ortho Research Foundation, New Jersey, U.S.A.; PMS: D.N. Kirk and P.M. Shaw, J.C.S. Perkin I, 1975, 2284; SK & F: Smith, Kline and French Laboratories, Philadelphia, U.S.A.; FS: F. Šorm, Prague; PT: P. Toft, Dept. of National Health and Welfare, Ottawa, Canada; MEW: M.E. Wolff, San Francisco, U.S.A.

<sup>d</sup>λ<sub>1</sub> indicates lowest wavelength limit of measurement (not necessarily a maximum or minimum in the c.d. curve).

<sup>e</sup>Prepared by Wittig reaction from 3β-hydroxy-des-D-13β(H)-androst-5-en-14-one, kindly provided by Dr. G. Anner, Ciba-Geigy, A.G., Basel.

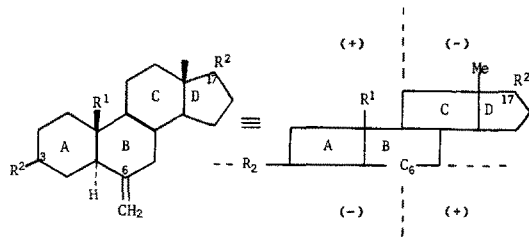
<sup>f</sup>Result of curve resolution: see text, p.2479.





(A20) R=H (androstane series)

(A21) R=OAc (cholestane series)

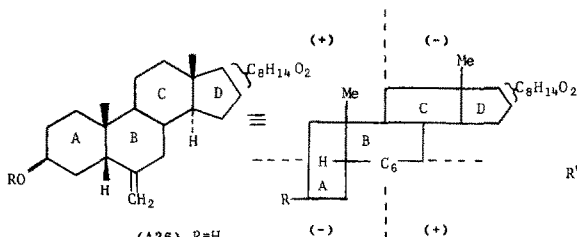


(A22) R<sup>1</sup>=R<sup>2</sup>=R<sup>3</sup>=H

(A23) R<sup>1</sup>=Me, R<sup>2</sup>=R<sup>3</sup>=H

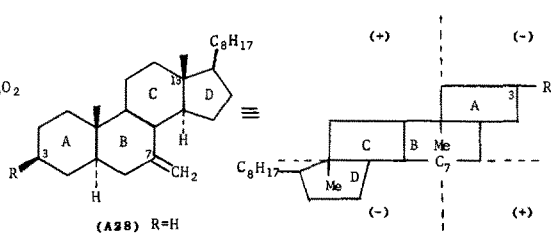
(A24) R<sup>1</sup>=Me, R<sup>2</sup>=H, R<sup>3</sup>=17β-C<sub>8</sub>H<sub>17</sub>

(A25) R<sup>1</sup>=Me, R<sup>2</sup>=OH, R<sup>3</sup>=17β-C<sub>8</sub>H<sub>17</sub>



(A26) R=H

(A27) R=Ac

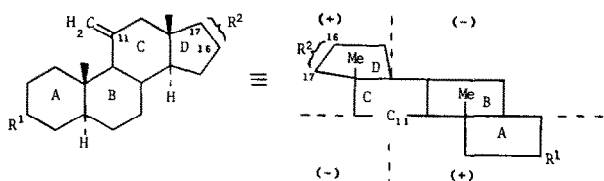


(A28) R=H

(A29) R=OH

(A30) R=OAc

(A31) R=H, ring D omitted, 13α-Me



(A32) R<sup>1</sup>=(MeO)<sub>2</sub>, R<sup>2</sup>=17β-OH

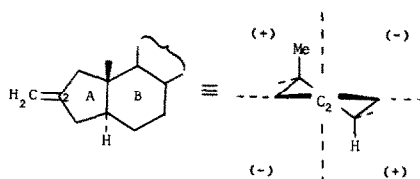
(A33) R<sup>1</sup>=O, R<sup>2</sup>=17β-O.CO.C<sub>2</sub>H<sub>5</sub>

(A34) R<sup>1</sup>=(MeO)<sub>2</sub>, R<sup>2</sup>=17β-O.CO.C<sub>2</sub>H<sub>5</sub>

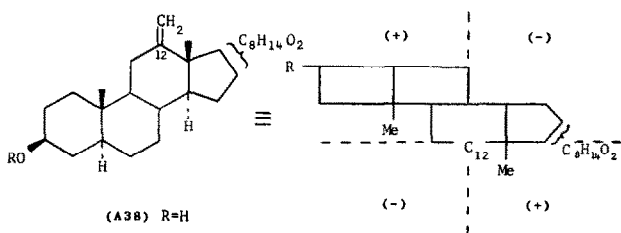
(A35) R<sup>1</sup>=H, R<sup>2</sup>=rings E+F of 25R-spirostan

(A36) R<sup>1</sup>=OH, R<sup>2</sup>=rings E+F of 25R-spirostan

(A37) R<sup>1</sup>=OAc, R<sup>2</sup>=rings E+F of 25R-spirostan

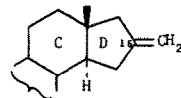


(A40) (androstane series)

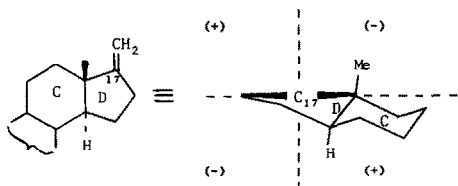


(A38) R=H

(A39) R=OAc

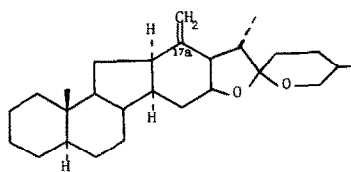


(A41) (octant diagram quasi-enantiomer of A40)

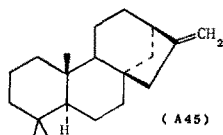


(A42) (5α-androstane series)

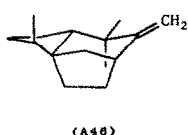
(A43) (5α-androstan-3β-ol)



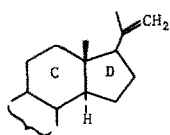
(A44)



(A45)



(A46)



(A47) (5α-pregnane)

(A48) (5β-pregnan-3β-ol)

compounds is a very large dissignate contribution (10–12 units) associated with the axial  $3\alpha$ -Me substituent in the 4-methylene compounds (A6 and A7); the effect is sufficient to reverse the sign of  $\Delta\epsilon$ , while not altering the wavelength  $\lambda_1$ . No explanation is apparent. Models suggest that the  $3\alpha$ -Me group is spatially related to the chromophore in much the same way as the  $13\beta$ -Me group in the 17 $\alpha$ -methylene-D-homo compound. A twisted conformation of ring A in A6 and A7 cannot be ruled out, or it may be significant that the methyl groups in question are attached to tertiary and quaternary C atoms, respectively. [Note the comparable dissimilarity of contributions of “ $\alpha$ ”-axial Me groups in trisubstituted olefins (p. 2496, and Fig. 9).]

An “ $\alpha$ ”-equatorial Me group may have a small effect; the two examples listed, the  $3\beta$ -methyl-4-methylene- (A8) and 14-methylene-des-D (A9) compounds show maxima of the same signs as their analogues lacking the extra Me group, although the Me group increments, estimated by comparisons with 4-methylene-5 $\alpha$ -androstane and 4-methylene-5 $\alpha$ -oestrane, respectively, are of opposite signs, so cannot be considered reliable.

Fétizon's 1-methylene-5 $\alpha$ -androstane (A10)<sup>12</sup> provides the only example of its type, with the third ring possibly projecting into a front octant.<sup>26,27</sup> Clearly this “third” ring makes no large contribution to  $\Delta\epsilon$ .

Those curves which show significant dichroism at the short-wavelength end of the spectrum (*ca.* 185 nm) all exhibited a “tail” of sign opposite to that at  $\lambda_1$ , but with  $\Delta\epsilon$  *ca.* 0 in the region of 188–190 nm ( $\lambda_2$ ). The reason for the virtual absence of a CD band at  $\lambda_2$  became apparent from a study of the 2-methylene-decalins (below). The strong “tail” of the curve presumably represents the beginning of the CD band at  $\lambda_3$ , centred well below 185 nm.

### Group 2

**2-Methylene-decalins (3).** The CD curves for this class are generally of composite character, comprising two overlapping bands of like sign (see Yogev *et al.*<sup>19</sup>).

After curve resolution, all the compounds resembling the 3-methylene-5 $\alpha$ -steroid type (A11–A17) give consignate  $\Delta\epsilon$  values close to 3 units at  $\lambda_1$ . “ $\alpha$ ”-Equatorial Me substituents have little or no effect at  $\lambda_1$ . 3-Methylene-5 $\beta$ -steroids (A20, A21) give curves of similar magnitudes to the 5 $\alpha$ -isomers, though of opposite sign (still consignate), suggesting that the presence of the “ $\beta$ ”-equatorial C(5)–C(6) bond is the main contributing factor in both the *cis* and the *trans* series. Third rings of the types represented by ring C in 3-methylene-5 $\alpha$ -steroids (3-methylene perhydrophenanthrene), or ring B in the 3'-methylene “pentacyclic” steroid (A14) (2-methylene perhydroanthracene type) have no measurable effect on  $\Delta\epsilon$  at  $\lambda_1$ . The remaining possibility for a third ring is in a 2-methyleneperhydrophenanthrene, represented by 2-methylene-5 $\alpha$ -androstane (A18), where the combined effects of ring C and the “ $\beta$ ”-axial 10 $\beta$ -Me group enhance  $\Delta\epsilon(\lambda_1)$  by some 7 units (consignate). This enhancement is compatible with an increment of about 5 units from the 10 $\beta$ -Me group (*cf.* 1-methylene decalins, above), and 2 units from ring C. Since the *spatial* relationship between the methylene group and ring C is the same for a 2-methylene as for a 4-methylene steroid, where an increment of 2 units was found for ring C, these estimates of structural contributions probably have general validity.

The curves at  $\lambda_2$  present a different picture. Where a maximum has been observed, it has the same sign as that at  $\lambda_1$ , as demonstrated by Yogev *et al.*<sup>19</sup> rather than the

opposite sign as proposed earlier by Fétizon and Scott.<sup>17</sup> The relatively large magnitude for a 3-methylene-5 $\alpha$ -steroid [ $\Delta\epsilon(\lambda_2) +5$  to  $+6$ ] is responsible for the  $\lambda_1$  part of the curve appearing only as a shoulder near 200 nm. (Yogev's values of  $\Delta\epsilon$ <sup>19</sup> are larger than ours, which agree more closely with the data reported by Fétizon<sup>12</sup>). The magnitude of  $\Delta\epsilon$  at  $\lambda_2$  is strongly influenced by further substitution, being almost doubled by the third ring in the methyleneperhydroanthracene analogue (A14); it is also nearly doubled by a 2 $\alpha$ -Me substituent (A15), but is reduced to zero by a 4 $\alpha$ -Me substituent (A16), occupying the “mirror-image” position. This unexpectedly large effect of “ $\alpha$ ”-equatorial substituents finds a parallel in 1,2-disubstituted ethylenes (p. 2488), and suggests an explanation for the absence of a CD maximum in the  $\lambda_2$  region for 1-methylene-*trans*-decalins (see above). The C–C bonds in the “second” ring of a 1-methylene-*trans*-decalin which seem most likely to influence the methylene group are those in the “ $\alpha$ ” and “ $\beta$ ”-equatorial positions with respect to the methylenecyclohexane ring, giving a structural fragment (5) similar to that found in the 4 $\alpha$ -methyl-3-methylene steroid (A16), where  $\Delta\epsilon(\lambda_2)$  is zero. Clearly the effect is a mutual cancellation of the contributions of the “ $\alpha$ ” and “ $\beta$ ” equatorial bonds, so that the 1-methylene-*trans*-decalins (2) also exhibit no Cotton effect at  $\lambda_2$ .

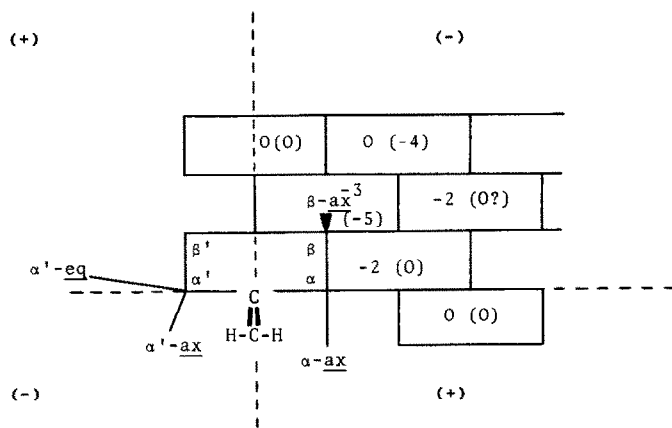
Figure 5 illustrates the estimated contributions ( $\delta\Delta\epsilon$ ) associated with individual rings and methyl substituents in methylene-decalin analogues, at both  $\lambda_1$  and  $\lambda_2$ .

### Group 3

**“Middle-ring” methylene compounds (4).** Four “all-*trans*” types are available (Table 2; A22–A25, A28–A39). The 6-methylene-5 $\alpha$ - and 12-methylene-5 $\alpha$ -steroidal ring systems are of *quasi*-enantiomeric type if the 5-membered nature of ring D be ignored. The similarity of sign and values of  $\Delta\epsilon$  at  $\lambda_1$  (*ca.* +4.4 and +2.5, respectively) can be accounted for if the 10 $\beta$ -Me group in the 6-methylene-5 $\alpha$ -androstane (A23) or cholestane (A24) is allotted a normal “ $\beta$ ”-axial contribution of +5 units, which would leave a small residual negative contribution for the ring system, opposite in sign to that of the 12-methylene compounds. Comparison of 6-methylene-5 $\alpha$ -oestrane (A22;  $\Delta\epsilon$  –0.3) with 6-methylene-5 $\alpha$ -androstane (A23;  $\Delta\epsilon$  +4.2) confirms the strong positive effect of the 10 $\beta$ -Me group.

The pair represented by 7-methylene-5 $\alpha$ -cholestane (A28) and 11-methylene-5 $\alpha$ -androstanes (A32–A34) are also *quasi*-enantiomeric, yet give weak CD bands of the same (negative) sign at  $\lambda_1$ . The 11-methylene system is complicated by the proximity of both the 13 $\beta$ - (“ $\beta$ ”-axial) Me group, which should make a positive contribution, and also the 10 $\beta$ -Me group. The latter must be supposed to make an even larger negative contribution to explain the observed effect, but this cannot be confirmed until a 19-nor 11-methylene derivative becomes available for comparison.

The 6-methylene-5 $\beta$ -spirostans (A26) and (A27) are particularly interesting. The *cis*-fusion of rings A and B gives the C(4)–C(5) bond the same relationship to the methylene group as the 3 $\alpha$ -methyl substituent has in the 3 $\alpha$ -methyl-4-methylene series, which showed unusual dissignate behaviour (above). The strongly positive (dissignate) effect of ring A in the 6-methylene 5 $\beta$ -isomer is further evidence that this apparent anomaly is a real effect, and is not due to some abnormal conformation of ring A in the 3 $\alpha$ -Me compounds.



Estimated effects of methyl substituents are as follows:-

	$\delta\Delta\epsilon$ at $\lambda_1$	$\delta\Delta\epsilon$ at $\lambda_2$
$\alpha$ -axial Me ( $\text{>C-Me}$ )	ca.0	ca.0
$\alpha'$ -axial Me ( $\text{>CHMe}$ )	+12 (dissignate)	-12 (consignate)
$\alpha'$ -equatorial Me	small	- 5 (dissignate)
$\beta$ -axial Me	- 5	ca.0

Fig. 5. Methylene-decalins. Octant projection showing estimated consignate contributions of rings to  $\Delta\epsilon$  values of extended methylene-decalin analogues:  $\delta\Delta\epsilon$  values at  $\lambda_1$  (ca. 200 nm), with  $\delta\Delta\epsilon$  values at  $\lambda_2$  (ca. 188 nm) in parentheses.

The only olefins in this sub-group showing a definite maximum at  $\lambda_2$  are those of the 6-methylene type. The others appear to show the beginning of the strong curve at  $\lambda_2$  (with sign opposite to that at  $\lambda_1$ ), which we have associated with the 1-methylene-*trans*-decalin fragment of structure. No quantitative treatment is possible with the present set of data.

### Summary

Consignate behaviour of nearly all structural components is the general rule at  $\lambda_1$  in this group of olefins. Even 6-methylene-5 $\alpha$ -androstane (**A23**), noted by Fétizon as an apparent exception, is dominated by the large consignate contribution of the 10 $\beta$ -Me group; it differs in this respect from 6-oxo-5 $\alpha$ -steroids, where the 10 $\beta$ -Me contribution to the  $n \rightarrow \pi^*$  transition is negligible compared with the negative contribution of ring C.<sup>27</sup> The only major apparent anomaly lies in the large dissignate effect of " $\alpha$ "-axial substituents in systems of the 3 $\alpha$ -methyl-4-methylene type. 11-Methylene steroids still present an unsolved problem.

Consignate behaviour, or obedience to a carbonyl-like octant rule, is shown also in the few known methylene cyclopentane analogues (e.g. 16- and 17-methylene-steroids; **A41-A43**), and in miscellaneous compounds including 20-methylenepregnanes (**A47, A48**) and phyllocladene (**A45**). The hydrocarbon prezizaene (**A46**) has been said to show "reverse-octant" behaviour,<sup>43</sup> but is not a good example because of the high degree of strain, and probable distortion from ideal geometry.

### Class B

*Cis*-1,2-Disubstituted ethylenes (Table 3). The available bicyclic and polycyclic olefins in this class may be divided broadly into four sub-groups according to bicyclic character. For convenience, these compounds are designated as derivatives of the parent octalins (**6**;  $\Delta^2$ ), (**7**;  $\Delta^1$ -*trans*) and (**8**;  $\Delta^1$ -*cis*); a few compounds of other types

are collected as the fourth group. (Steroid-like numbering is used for convenience.)

### Group 1

*trans*- $\Delta^2$ -Octalins (**6**). The value of  $\Delta\epsilon(\lambda_1)$  is about  $+3.5 \pm 1$  (199  $\pm 1$  nm) for compounds (**B3-B8**). The positive sign is characteristic of the sense of twist of the cyclohexene ring (*P*-helicity<sup>44</sup> with respect to the  $C_2$  axis of symmetry of the cyclohexene ring). Alternatively, the sign corresponds to consignate behaviour of " $\alpha$ "-axial C-H bonds.<sup>7</sup>

The presence of a 4 $\alpha$ -Me substituent (**B8**; " $\alpha$ "-equatorial) does not have any notable effect at  $\lambda_1$ , but 4,4-dimethyl substitution (**B9, B10**) appears slightly to reduce  $\Delta\epsilon$ , suggesting that the " $\alpha$ "-axial 4 $\beta$ -Me group has a weakly dissignate effect. 4(*R*)-Methylcyclohexene (**B1**) can be regarded as belonging to the same group of olefins, with the ring predominantly in the half-chair form (**9**), like the cyclohexene ring in *trans*- $\Delta^2$ -octalins of steroid-like configuration (**10**); a small proportion (perhaps 20%) of the inverted half-chair conformation (*ax*-Me) would explain the low value of  $\Delta\epsilon$ .

It appears that a cyclohexene ring in the conformation **9** (*P*-helicity) contributes about  $+3.5 \pm 1$  to  $\Delta\epsilon$  at  $\lambda_1$  (*M*-helicity  $-3.5 \pm 1$ ). Additional rings of a *trans*- $\Delta^2$ -octalin derivative have little if any effect. There is no appreciable CD at  $\lambda_2$  in this group of compounds except for the 4 $\alpha$ -methyl compound (**B8**) (see below).

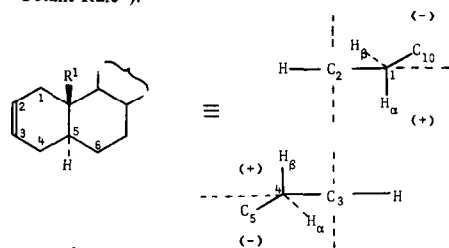
### Group 2

*trans*- $\Delta^1$ -Octalins (**7**). This group of compounds is considered to include all those structures (**B11-B15**) in which another ring is fused to the cyclohexene ring by *quasi*-equatorial bonds " $\alpha$ " and " $\beta$ " to the olefinic bond (**11**). It is extended to embrace compounds **B16-B23** which include the tricyclic dodecahydrophenanthrene structural fragment (**12**), found in steroidal 6-enes; steroidal 11-enes are included here, for although ring D is 5-membered,

Formulae of Compounds (see Table 3 for names and CD data).

Octant diagrams give the view from the midpoint of the C=C bond.

Signs indicated for octants are those which would correspond to *consignate* behaviour (right-handed "Octant Rule").



(B3) R<sup>1</sup>=Me (bicyclic)

(B4) R<sup>1</sup>=Me (6,6-Me<sub>2</sub>, bicyclic)

(B5) R<sup>1</sup>=CH<sub>2</sub>OH (bicyclic)

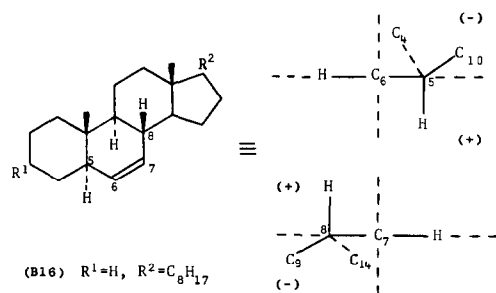
(B6) R<sup>1</sup>=Me (cholestane)

(B7) R<sup>1</sup>=Me (25R-spirostan)

(B8) R<sup>1</sup>=Me (4α-Me, 17β-acetoxy-androstane)

(B9) R<sup>1</sup>=Me (4,4-Me<sub>2</sub>, lupane)

(B10) R<sup>1</sup>=Me (4,4-Me<sub>2</sub>, cholestane)

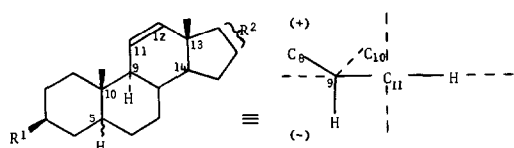


(B16) R<sup>1</sup>=H, R<sup>2</sup>=C<sub>8</sub>H<sub>17</sub>

(B17) R<sup>1</sup>=β-OH, R<sup>2</sup>=C<sub>8</sub>H<sub>17</sub>

(B18) R<sup>1</sup>=α-OH, R<sup>2</sup>=C<sub>8</sub>H<sub>17</sub>

(B19) R<sup>1</sup>=R<sup>2</sup>=β-OH



(B21) R<sup>1</sup>=H, R<sup>2</sup>=rings E+F of 5α,25R-spirostan

(B22) R<sup>1</sup>=OH, R<sup>2</sup>=rings E+F of 5α,25R-spirostan

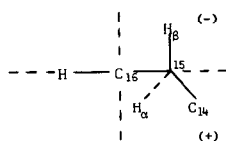
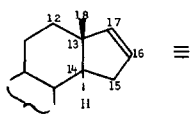
(B23) R<sup>1</sup>=OH, R<sup>2</sup>=17β-COOMe (5α)



(B27)



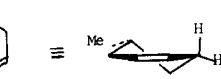
(B28)



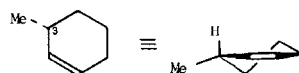
(B29) (5α-androstane)

(B30) (5α-androstan-3β-ol)

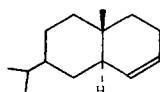
(B31) (5β-androstan-3α-ol)



(B1)

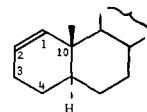


(B2)



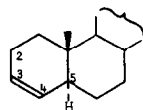
(B11)

(octant diagrams of enantio-B14 type)



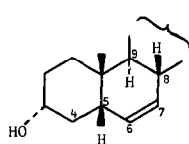
(B12) (cholestane)

(B13) (4,4-Me<sub>2</sub>-cholestane) (octant diagrams resemble B14, with Me in place of H<sub>β</sub>)

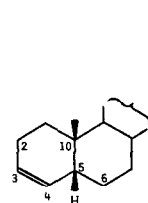
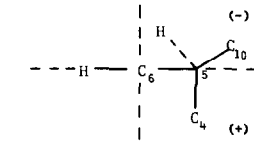


(B14) (cholestane)

(B15) (androstan-17β-ol)



(B20) (octant diagram for C<sub>7</sub> as B16)



(B24) (androstan-17β-ol)

(B25) (17β-AcO-androstane)

(B26) (17α-Me-androstan-17β-ol)

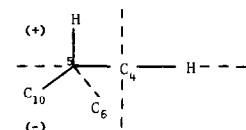
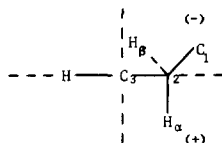


Table 3. CD data for *cis*-1,2-disubstituted ethylenes

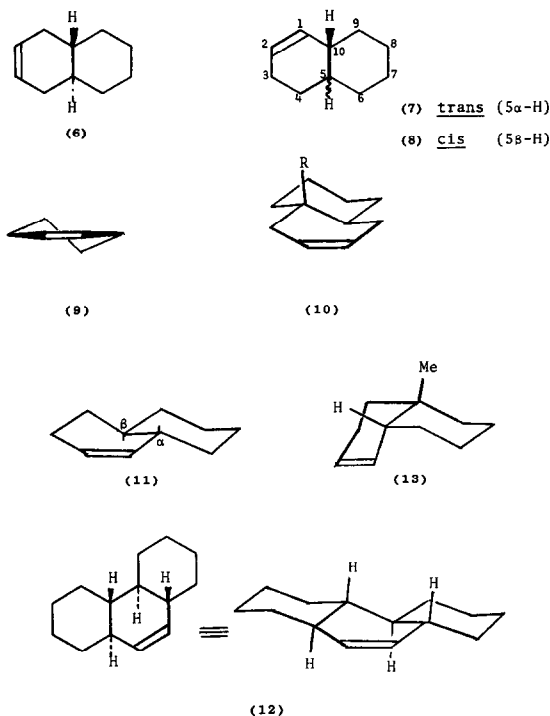
No.	Compound	SOLVENT: Methanol			Hexane			"Calculated"		Source of compounds <sup>e</sup>	
		C.d. ref. <sup>a</sup>	$\Delta\epsilon$	$\lambda$ (nm)	$\Delta\epsilon$	$\lambda_1$ (nm)	$\Delta\epsilon$	$\lambda_2$ <sup>d</sup> (nm)	$\Delta\epsilon^b$ at $\lambda_1$ $\lambda_2$		
<u>Cyclohexenes</u>											
B1	4(R)-Methylcyclohexene	S			+1.8	198	-	-	+1.8 <sup>e</sup>	0	
B2	3(R)-Methylcyclohexene	S (IX)			ca.-8.4	199.5	+17	185	-3 <sup>e</sup>	+16(185)	
<u>trans-<math>\Delta^2</math>-Octalin types</u>											
B3	9(S),10(S)-9-Methyl- $\Delta^2$ -octalin	W	+3.2m	199	+3.7	199	-	-	+3	0	JH
B4	9(S),10(R)-5,5,9-Trimethyl- $\Delta^2$ -octalin	W	+2.0m	200	+2.8	200	-0.8	192	+3	0	JH
B5	9(R),10(S)-9-Hydroxymethyl- $\Delta^2$ -octalin	W	+3.5	196					+3	0	JH
B6	5 $\alpha$ -Cholest-2-ene	S			+3.6	198	-	-	+3	0	
B7	5 $\alpha$ ,25R-Spirost-2-ene	{W {S	+1.65	202	+3.15 +4.3	197 200	+3.15	184	+3	0	JE
B8	4 $\alpha$ -Methyl-5 $\alpha$ -androst-2-en-17 $\beta$ -ol, 17-acetate	W			+3.1	199	-9.8	185	+4	-17(185)	DNK
B9	Lup-2-ene	W			+1.8	197	ca.0	183	+2.5	-6(185)	TGH
B10	4,4-Dimethyl-5 $\alpha$ -cholest-2-ene	W			+2.8	200	ca.0	183	+2.5	-6(185)	JL
<u>trans-<math>\Delta^1</math>-Octalin types</u>											
B11	3(S),9(S),10(R)-3-isopropyl-9-methyl- $\Delta^1$ -octalin	W			+4.6	202	-18.0	185	+4	-17	FF & AT
B12	5 $\alpha$ -Cholest-1-ene	{S {W			-2.9 -1.95	200 201	+2.2 +5.8	190 184	-2.5	+4(190) +6(185)	JH
B13	4,4-Dimethyl-5 $\alpha$ -cholest-1-ene	W			sh	ca.195	+6.4	187	-2.5	+6(185)	JL
B14	5 $\alpha$ -Cholest-3-ene	S			-4.7	202	+13.6	187	-4	+15(187)	
B15	5 $\alpha$ -Androst-3-en-17 $\beta$ -ol	S,L			-3.5	202	-	-	-4	+17(185)	
B16	5 $\alpha$ -Cholest-6-ene	{W {S	-8.0!	198	[ca.+8	198	-31.2m -3.1	187] <sup>f</sup> 187	+5	-34(185)	JH
B17	5 $\alpha$ -Cholest-6-en-3 $\beta$ -ol	W	-12.1!	200	-	-	-18.3	191	+5	-18(191) -34(185)	DNK
B18	5 $\alpha$ -Cholest-6-en-3 $\alpha$ -ol	W	-5.9sh -10.0!	206 201	[+2.4	ca.205	-26.2	190] <sup>f</sup>	+5	-24(190) -34(185)	DNK
B19	5 $\alpha$ -Androst-6-ene-3 $\beta$ ,17 $\beta$ -diol	S,L	-2.5	187					+5	-32(187)	
B20	5 $\beta$ -Cholest-6-en-3 $\alpha$ -ol	W			sh [+2.2	200 198	-7.8m -11	190 188] <sup>f</sup>	+2.5	-6(185)	DRAL
B21	5 $\alpha$ ,25R-Spirost-11-ene	W	-4.2!	200	-8.2	197	+9.5	185	-3.5 <sup>g</sup>	+23(185) <sup>g</sup>	JE
B22	5 $\alpha$ ,25R-Spirost-11-en-3 $\beta$ -ol	{W {S			-6.2m -7.8	196 197.5			-3.5 <sup>g</sup>	+23(185) <sup>g</sup>	JE
B23	3 $\beta$ -Hydroxy-5 $\beta$ -eti-11-enic acid, methyl ester	S			-1.5	202	+6.4	189	-3.5 <sup>g</sup>	+18(189) <sup>g</sup> +23(185)	
<u>cis-<math>\Delta^1</math>-Octalin types</u>											
B24	5 $\beta$ -Androst-3-en-17 $\beta$ -ol	W	+3.6m	203	+4.9m	200	-6.6	192	+5	-9.5(185)	DNK
B25	5 $\beta$ -Androst-3-en-17 $\beta$ -ol 17-acetate	W	-	-	+5.8	201	-7.4	188	+5	-9.5(185)	DNK
B26	17 $\alpha$ -Methyl-5 $\beta$ -androst-3-en-17 $\beta$ -ol	W	-	-	+5.3	201	-9.1	187	+5	-9.5(185)	DNK
<u>Other Cycloalkenes</u>											
B27	3(R)-Methylcyclobutene	R & D			-5.0sh -6.8	193 191					
B28	3(R)-Methylcyclopentene	R & D			(-)	188					
B29	5 $\alpha$ -Androst-16-ene	W	-1.6!	195	-1.9m	192					JH
B30	5 $\alpha$ -Androst-16-en-3 $\beta$ -ol	{W {S	-2.0!	200	-2.4m -2.6	193 195					JH
B31	5 $\beta$ -Androst-16-en-3 $\alpha$ -ol	{W {S	-2.5m	197	-2.8m -2.8	194 195					JH

<sup>a</sup>See Table 2, footnote a. <sup>b</sup>Calculated from data in Figure 7. Wavelengths in parentheses refer to Figure 6.

<sup>c</sup>See Table 2, footnote c. <sup>d</sup>Values at lowest accessible wavelength unless otherwise indicated: see text,

and Figure 6. <sup>e</sup>The "calculated" value assumes a rigid chair conformation. <sup>f</sup>Result of curve resolution: see text.

<sup>g</sup>The "calculated" values assume a six-membered ring D.



these compounds show close similarities (*quasi*-enantiomeric) to the 6-enes.

Values of  $\Delta\epsilon$  at  $\lambda_1$ , sometimes obtained only by curve resolution, are similar to, or perhaps a little larger than, those found for compounds of Group 1. Comparison of the  $5\alpha$ -steroidal-1-enes (**B12** and **B13**) with the " $5\alpha$ -3-ene" types (**B11**, **14** and **15**) suggests that the " $\alpha$ "-axial  $10\beta$ -Me group has a small dissignate effect (*ca.* +1.5). The  $\Delta^6$ - and  $\Delta^{11}$ -unsaturated steroids show bands at  $\lambda_1$  with signs determined by the sense in which the cyclohexene ring is twisted, but the magnitude of  $\Delta\epsilon$  is somewhat larger for the  $\Delta^{11}$  compounds; this could result from the change in size (and strain) of ring D, and/or the presence of a  $17\beta$ -side-chain, so  $\Delta\epsilon$  values for  $\Delta^{11}$  compounds are not regarded as typical.

The outstanding feature of "*trans*- $\Delta^1$ -octalin" compounds is a very strong CD band at  $\lambda_2$ , which is sometimes so large that its tail almost obscures the weaker band near 200 nm ( $\lambda_1$ ). The Cotton effect at  $\lambda_2$  is consignate with respect to " $\alpha$ "-*quasi*-equatorial substitution of the cyclohexene ring [e.g. the  $10(9)$ -bond in formula **7**], a structural feature which all these compounds have in common as a consequence of the location of the adjoining saturated ring. Two C-C bonds of " $\alpha$ "-*quasi*-equatorial type occur in  $\Delta^6$ - and  $\Delta^{11}$ -unsaturated steroids. Other compounds which have " $\alpha$ "-*quasi*-equatorial substitution and share the characteristic of a strong CD band at  $\lambda_2$  are the  $4\alpha$ -methyl- $\Delta^2$ -compound (**B8**) considered under Group 1, and  $3(R)$ -methylcyclohexene (**B2**). We therefore attribute the large Cotton effect at  $\lambda_2$  to the presence of *quasi*-equatorial allylic substitution. We hope to comment on the nature of this effect in a later paper (see also p. 2505).

The CD curves available did not exhibit clear maxima below 195 nm, but values of  $\Delta\epsilon(\lambda_2)$  at the shortest wavelengths for which measurements were possible fell on a reasonably smooth Gaussian curve (Fig. 6) when plotted against limiting wavelength. The maximum of the curve is at or below 185 nm, where  $\Delta\epsilon$  has a value of

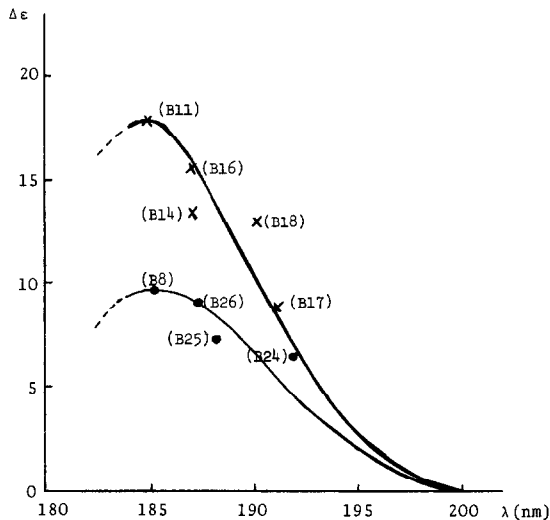


Fig. 6. Chiral cyclohexene analogues (*cis*-disubstituted ethylenes). Plots of limiting value of  $\Delta\epsilon$  (at shortest wavelength measured) vs wavelength ( $\lambda_2$ ) for compounds of the  $\Delta^1$ -octalin types (**7**) and (**8**). —X—X— *trans*-fused series (**7**); ——— *cis*-fused series (**8**). Entries in Table 3 indicated in parentheses.— see text, this page.

about 17 units (consignate with respect to " $\alpha$ "-*quasi*-equatorial groups). The points on the graph representing  $\Delta^6$ -compounds are plotted at *half* the observed limiting  $\Delta\epsilon$  value, so that the curve represents the contribution of one " $\alpha$ "-*quasi*-equatorial (allylic) C-C bond to  $\Delta\epsilon$  at  $\lambda_2$ . An " $\alpha$ " *quasi*-axial C-C bond ( $10\beta$ -Me in  $\Delta^1$ , or  $4\beta$ -Me in  $\Delta^2$ -steroids) seems to reduce the value of  $\Delta\epsilon(\lambda_2)$  by introducing a consignate effect which largely but not wholly counteracts that of the *quasi*-equatorial C-C bond. The value can be estimated only very roughly from data available, but may be about 11 units at 185 nm, with correspondingly lower values observed at longer wavelengths when the maximum of the  $\lambda_2$  curve is not reached.

$5\beta$ -Cholest-6-en- $3\alpha$ -ol (**B20**) is interesting in showing a diminished CD band at  $\lambda_2$  compared with the  $5\alpha$ -isomer. Rings B and C of the molecule are fused in the normal *trans* sense, and would give a strongly negative CD band, but the A/B fragment is a "*cis*- $\Delta^1$ -octalin" (see below), with the C(4)-C(5) bond *quasi*-axial to ring B, and would be expected to give a positive (consignate) contribution somewhat smaller than in the *trans*- $\Delta^1$ -octalins, leaving a net negative effect as observed.

### Group 3

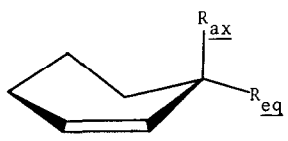
*cis*- $\Delta^1$ -Octalins (**8**). *cis*-Fused systems are represented by the  $5\beta$ - $\Delta^3$ -compounds (**B24**-**B26**), and in a somewhat different form by the  $5\beta$ - $\Delta^6$ -compound (**B20**), mentioned above. Unlike the  $5\beta$ - $\Delta^6$ -compound, the cyclohexene ring in the  $5\beta$ - $\Delta^3$ -unsaturated steroids is fused to the adjoining ring in such a manner that the C(5)-C(6) bond is *quasi*-equatorial (**13**). The sign of the CD band at  $\lambda_1$  is again dominated by the sense of twist of ring A, giving  $\Delta\epsilon$  the same sign as is found for compounds of similar chirality in Group 2, though with a slightly larger  $\Delta\epsilon$  value. The enhancement of  $\Delta\epsilon$  may perhaps indicate a small dissignate contribution from the C(5)-C(6) bond; inspection of a molecular model shows that this bond has somewhat less equatorial and more axial character than the same bond in a  $5\alpha$ - $\Delta^3$ -unsaturated steroid. We have

already noted that a *quasi*-axial allylic bond makes a significant dissignate contribution at  $\lambda_1$  to compounds of either Groups 1 or 2.

The strong CD band at  $\lambda_2$  in compounds of Group 3 is similar in character to that found in Group 2 (consignate), but is of smaller magnitude ( $\Delta\epsilon$  estimated as 9.5 units at 185 nm: see Fig. 6). The smaller value is consistent with the conformational character of the " $\alpha$ " (allylic) C–C bond, which tends more towards *quasi*-axial than *quasi*-equatorial character (see discussion under Group 2, above).

#### Summary for Groups 1–3

The findings for compounds of the cyclohexene type belonging to these three groups within the class of *cis*-1,2-disubstituted ethylenes are summarised (for the enantiomer with *P*-helicity) in Fig. 7. The increments indicated in Fig. 7, together with the graphical relationships between  $\Delta\epsilon(\lambda_2)$  and wavelength for incomplete curves (Fig. 6) have been used to derive the "calculated" values of  $\Delta\epsilon$  listed in the final two columns of Table 3.



Structural feature	$\delta\Delta\epsilon$ at $\lambda_1$	$\delta\Delta\epsilon$ at $\lambda_2$
Chiral Ring ( $R_{ax}=R_{eq}=H$ )	+3	ca.0
<u>Increment for:-</u>		
<u>quasi</u> -axial $CH_3$ or $CH_2$ ( $R_{ax}$ )	-1.5 (dissignate)	+11 (185 nm) (consignate)
<u>quasi</u> -equatorial $CH_3$ or $CH_2$ ( $R_{eq}$ )	+1 (dissignate)	-17 (185 nm) (consignate)

Fig. 7. Chiral cyclohexene derivatives.

#### Group 4

*Miscellaneous cycloalkenes.* (Compounds **B27–B31**). The single CD band observed between 190 and 200 nm does not belong clearly to either  $\lambda_1$  or  $\lambda_2$ , but the dissignate behaviour of the Me groups in 3-methylcyclobutene and 3-methylcyclopentene suggests that it is  $\lambda_1$ . The observed negative CD band for steroidal-16-enes may be dominated by similar dissignate behaviour of the 18-Me group. It would be unwise, however, to use the data except for empirical comparison with closely analogous structures. Insufficient compounds were available to allow the separation of contributions due to distinct structural features for compounds of fused-cyclopentene type.

#### Class C

*Trisubstituted ethylenes* (Table 4). Trisubstituted olefins are exceptional in being the only class with no local symmetry elements, other than the plane defined by the two doubly-bonded carbon atoms and the four attached atoms (Fig. 8). Allylic (" $\alpha$ ") substitution generally destroys even this symmetry. The three C atoms attached to the olefinic carbons are therefore regarded as non-equivalent in the following analysis. For reference, we describe them as being *cis*-, *trans*- or *gem*-, respectively, to the olefinic hydrogen atom (Fig. 8).

It is reasonable to expect the influence of allylic

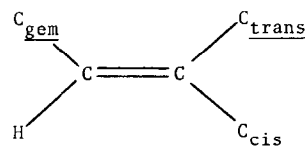
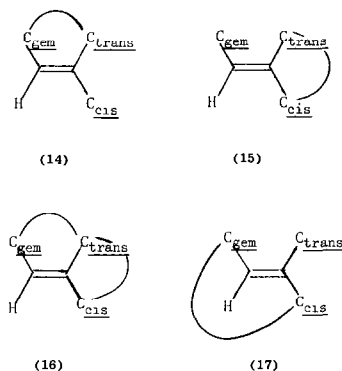


Fig. 8. Designations of allylic positions in a trisubstituted-ethylene derivative.

substitution on chiroptical properties to depend upon which of the three carbon atoms carries the substituent. This is found to be a key feature of trisubstituted olefins.

Semi-rigid cyclic compounds can be of four types:

- cis*-cycloalkene (**14**), where  $C_{gem}$  and  $C_{trans}$  are linked in a ring, and  $C_{cis}$  is an alkyl substituent;
- exocyclic alkylidene (**15**), where  $C_{trans}$  and  $C_{cis}$  are linked in a ring, and  $C_{gem}$  is an alkyl substituent;
- bicyclic (**16**), where *both* rings of the types classified under (i) and (ii) are present;
- trans*-cycloalkene (**17**), where  $C_{gem}$  and  $C_{cis}$  are linked in a ring.



Only types (i), (ii) and (iii) are represented among the present compounds, *trans*-cycloalkenes<sup>9,18</sup> being rare.

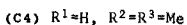
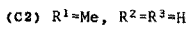
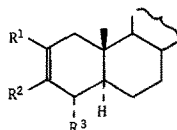
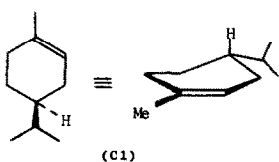
#### Group 1

*Cycloalkenes* (compounds **C1–C12**). Almost all the compounds in this group showed a CD band in the range 200–210 nm ( $\lambda_1$ ). The 2- and 3-methyl-5 $\alpha$ -cholest-2-enes (**C2** and **C3**) agree in sign of  $\Delta\epsilon$  with 5 $\alpha$ -cholest-2-ene itself (*P*-helicity), whereas *S*-(-)-limonene (**C1**), with a *quasi*-enantiomeric cyclohexene ring (*M*-helicity), gave a curve of opposite sign at  $\lambda_1$ . The partial structure (**18**) must be responsible for the positive CD at  $\lambda_1$ ; the differences in magnitude of  $\Delta\epsilon$  possibly reflect relatively minor contribu-

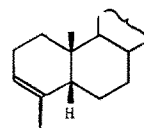
Formulae of Compounds (see Table 4 for names and CD data).

Octant diagrams give the view from the mid-point of the C=C bond.

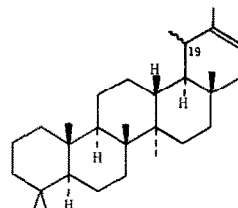
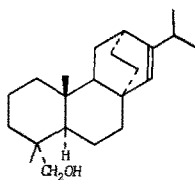
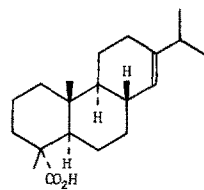
Signs indicated for octants are those which would correspond to *consignate* behaviour (right-handed "Octant Rule").



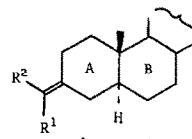
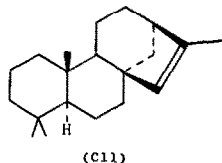
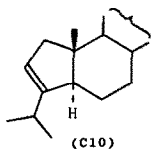
(octant diagrams for C2 and C3 resemble those for B3)



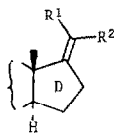
(octant diagrams similar to B24)



(C9) 19 $\alpha$ -Me



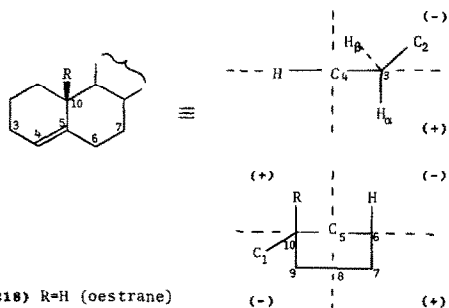
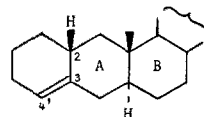
(C14)  $R^1=H, R^2=Me$



(C16)  $R^1=H, R^2=Me$



(C17)



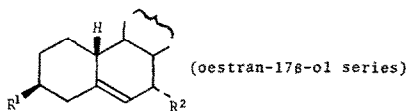
(C19) K=H (oestrane-17 $\beta$ -ol)

(C21) R=Me (cholestane)

(C22) R=Me (7 $\beta$ -OH, cholestane)

(C23) R=Me (7 $\alpha$ -OH, cholestane)

(C24) R=Me (3 $\alpha$ -CF<sub>3</sub>, 17 $\alpha$ -Me-androstan-17 $\beta$ -ol)



(C26)  $R^1=R^2=H$  (17 $\alpha$ -Me)

(C27)  $R^1=R^2=H$  (17 $\alpha$ -Et)

(C28)  $R^1=C1, R^2=H$  (17 $\alpha$ -Me)

(C29)  $R^1=C1, R^2=H$  (17 $\alpha$ -Et)

(C30)  $R^1=H, R^2=Me$

(C31)  $R^1=C1, R^2=Me$  (17 $\alpha$ -Et)

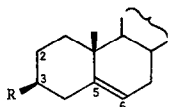
(C32)  $R^1=OH, R^2=H$  (cholestane series)

(octant diagrams of enantio-C18 type, with H<sub>3 $\alpha$</sub>  replaced by Me when R<sup>2</sup>=Me)

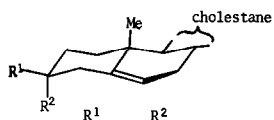


Table 4. CD data for trisubstituted ethylenes

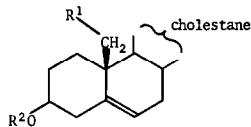
No.	Compound	SOLVENT: Methanol		Hexane (or cyclohexane)		"Calculated"		Source of compound <sup>c</sup>			
		C.d. ref. <sup>a</sup>	$\Delta\epsilon$	$\lambda_1$	$\lambda_2$	$\lambda_2$ and/or $\lambda_3$ <sup>d</sup>	$\Delta\epsilon^b$ at				
			$\lambda$ (nm)	$\Delta\epsilon$	$\lambda$ (nm)	$\Delta\epsilon$	$\lambda$ (nm)	$\lambda_1$	$\lambda_2$		
<u>endoCyclic (1-alkylcycloalkene types)</u>											
<u>(Cyclohexenes)</u>											
C1	S(-)-Limonene	S		- 2.3	210	+ 2!	198!	- 2.5	0.0		
C2	2-Methyl-5 $\alpha$ -cholest-2-ene	W	+ 1.25m	206	+ 1.4m	205	+ 2.7	185! ( $\lambda_3$ ?)	+ 2.5	0.0	JH
C3	3-Methyl-5 $\alpha$ -cholest-2-ene	{W S}	+ 3.6m	202	+ 3.7m + 4.1	202 200			+ 2.5	0.0	JH
C4	3,4 $\alpha$ -Dimethyl-5 $\alpha$ -cholest-2-ene	W	+ 2.3m	207	+ 3.7m	207	- 2.6m	188	+ 3.5	- 3	JL
C5	4,17 $\alpha$ -Dimethyl-5 $\beta$ -androst-3-en-17 $\beta$ -ol	W	+ 2.4m	210	+ 2.8m	205			+ 3.5	- 3	DNK
C6	Abiet-13-en-18-oic acid	S			- 1.5	208			- 2.5	0.0	
C7	8 $\alpha$ ,12 $\alpha$ -Ethanoabiet-13-en-18-ol	W	- 0.95 + 3.06!	215 202!	- 1.5m	210	+ 5.2!	197!	? ?	? ?	
C8	18 $\alpha$ -Urs-20-ene	W			-	-	+ 9.3m	195	? (+)?		TGH
C9	18 $\alpha$ ,19 $\beta$ (H)-Urs-20-ene	W			+ 4.45m	203	- 3.0!	189!	+ 3.5	- 3	TGH
<u>(Miscellaneous rings)</u>											
C10	3-Isopropyl-A-nor-5 $\alpha$ -cholest-2-ene	W			-10.7	210	+ 7.6!	186! ( $\lambda_3$ ?)	(-)	(+)	JL
C11	Kaur-15-ene (isophyllocladene)	S			+12.4	209	- 1.15!	190!	? ?		
C12	(+) $\alpha$ -Pinene	S			+ 1.2	219	- 2.7!	190!	? ?		
<u>Ethylidene cycloalkanes</u>											
C13	cis-(Z)-3-Ethylidene-5 $\alpha$ -cholestane	W <sup>e</sup>			- 6.0	212	+11.2	194	- 7	+ 9	RJM/DNK
C14	trans-(E)-3-Ethylidene-5 $\alpha$ -cholestane	W <sup>e</sup>			+ 8.6	208	- 8.0	185	+ 7	- 9	RJM/DNK
C15	cis-(Z)-Pregn-17(20)-ene	F & S					- 3.8	197	? ?		
C16	trans-(E)-Pregn-17(20)-ene	F & S			- 0.2	214	+ 4.6	193	? ?		
C17	3 $\beta$ -Hydroxy-D-homo-5 $\alpha$ -pregn-17 $\alpha$ (20)-ene (unknown configuration at C-20)	W			+ 2.0	206	- 3.0	185	+ 4 for cis(Z) configuration + 7 for trans(E) configuration	- 4 - 9	RJM
<u><math>\Delta^1(9)</math>-Octalin types</u>											
<u>(4-enes)</u>											
C18	Oestr-4-ene	W			+ 4.1	210	- 4.0	192	+ 5	- 4	DNK
C19	Oestr-4-en-17 $\beta$ -ol	W	+ 3.3m	210	+ 4.8	211	- 7.6	190	+ 5	- 6 <sup>f</sup>	HPdeJ
C20	2 $\alpha$ ,3-Tetramethylene-5 $\alpha$ -cholest-4'(3)-ene	W			+ 5.7	212	- 5.0!	185! ( $\lambda_3$ ?)	+ 5	- 4	DNK
C21	Cholest-4-ene	{W S}	- 5.8!	200!	- 8.6m	200	+11.6!	184! ( $\lambda_3$ ?)	- 6	+11	DNK
					- 8.4	202	+ 8.4!	185! ( $\lambda_3$ ?)			
C22	Cholest-4-en-7 $\beta$ -ol	W			- 5.3	198			- 3.5	+ 1.5	DHRB
C23	Cholest-4-en-7 $\alpha$ -ol	W			-10.5	199	+ 6.3!	190!	- 7.5	+19	DHRB
C24	17 $\alpha$ -Methyl-3 $\alpha$ -trifluoromethyl-androst-4-en-17 $\beta$ -ol	W			- 9.8	191			(-)	?	MEW
<u>(5-enes)</u>											
C25	Oestr-5-en-17 $\beta$ -ol	W	- 3.2	210	- 5.4m	207	+ 1.7m	194 ( $\lambda_2$ )	- 5	+ 2 <sup>f</sup>	HPdeJ
							- 2.0!	184! ( $\lambda_3$ )			
C26	17 $\alpha$ -Methyloestr-5-en-17 $\beta$ -ol	W	{- 4.2m + 1.1	209 198	- 5.4m	208	+ 3.3m	196 ( $\lambda_2$ )	- 5	+ 2 <sup>f</sup>	HPdeJ
C27	17 $\alpha$ -Ethylloestr-5-en-17 $\beta$ -ol	W	- 4.0m	209	- 4.3m	208	+ 1.2m	195 ( $\lambda_2$ )	- 5	+ 2 <sup>f</sup>	HPdeJ
							- 2.6!	185! ( $\lambda_3$ )			
C28	3 $\beta$ -Chloro-17 $\alpha$ -methyloestr-5-en-17 $\beta$ -ol	W	- 7.85	207	- 9.9m	204	+ 2.8	191 ( $\lambda_2$ )	-10	+ 5 <sup>f</sup>	HPdeJ
							- 2.4!	184! ( $\lambda_3$ )			



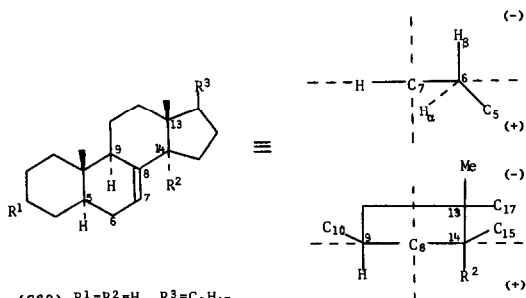
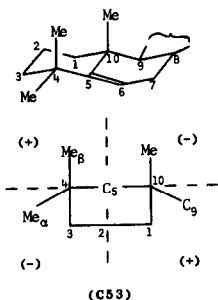
- (c33) R=H (tricyclic)  
 (c34) R=Cl (tricyclic)  
 (c35) R=H (androstane)  
 (c36) R=H (D-homoandrostane)  
 (c37) R=H (cholestane)  
 (c38) R=H (2 $\alpha$ -OH, cholestane)  
 (c39) R=H (2 $\beta$ -OH, cholestane)  
 (c54) R=H (androstan-17 $\beta$ -ol)  
 (c55) R=OH (androstane)  
 (c56) R=OH (17 $\alpha$ -Me-androstan-17 $\beta$ -ol)  
 (c57) R=OH (17 $\alpha$ -HOCH<sub>2</sub>CH<sub>2</sub>, 17 $\beta$ -OH)  
 (c58) R=HOCH<sub>2</sub>CH<sub>2</sub>O (cholestane)  
 (c59) R=OH (25R-spirostan)  
 (octant diagrams of enantio-c21 type; R=Me)



- (c40) OH H  
 (c41) OAc H  
 (c45) H OH  
 (c46) H OAc  
 (c47) Cl H  
 (c48) H Cl  
 (c49) F H  
 (c50) -OCH<sub>2</sub>CH<sub>2</sub>O-  
 (c51) Me OH  
 (c52) OH Me



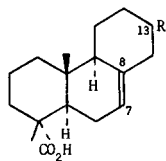
- (c42) R<sup>1</sup>=Me, R<sup>2</sup>=H  
 (c43) R<sup>1</sup>=OH, R<sup>2</sup>=Ac  
 (c44) R<sup>1</sup>=OMs, R<sup>2</sup>=Ac



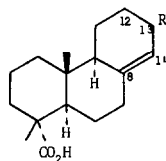
- (c60) R<sup>1</sup>=R<sup>2</sup>=H, R<sup>3</sup>=C<sub>8</sub>H<sub>17</sub>  
 (c61) R<sup>1</sup>= $\beta$ -OH, R<sup>2</sup>=H, R<sup>3</sup>=C<sub>8</sub>H<sub>17</sub>  
 (c62) R<sup>1</sup>= $\alpha$ -OH, R<sup>2</sup>=H, R<sup>3</sup>=C<sub>8</sub>H<sub>17</sub>  
 (c63) R<sup>1</sup>=(MeO)<sub>2</sub>, R<sup>2</sup>=H, R<sup>3</sup>=C<sub>8</sub>H<sub>17</sub>  
 (c64) R<sup>1</sup>=R<sup>2</sup>=H, R<sup>3</sup>=C<sub>9</sub>H<sub>19</sub>  
 (c65) R<sup>1</sup>=H, R<sup>2</sup>=Me, R<sup>3</sup>=C<sub>8</sub>H<sub>17</sub> (4,4-Me<sub>2</sub>)

Table 4. (Contd.)

No.	Compound	SOLVENT: C.d. ref. <sup>a</sup>	Methanol		Hexane (or cyclohexane)			"Calculated" $\Delta\epsilon^b$ at		Source of compound <sup>c</sup>	
			$\Delta\epsilon$	$\lambda$ (nm)	$\Delta\epsilon$	$\lambda$ (nm)	$\lambda_1$	$\lambda_2$ and/or $\lambda_3$ <sup>d</sup>	$\lambda_1$		$\lambda_2$
C29	3 $\beta$ -Chloro-17 $\alpha$ -ethyloestr-5-en-17 $\beta$ -ol	W	- 6.95	206	-11.0m	204	+ 2.4m	191 ( $\lambda_2$ ) - 1.8! 185! ( $\lambda_3$ )	-10	+ 5 <sup>f</sup>	HPdeJ
C30	7 $\alpha$ -Methyloestr-5-en-17 $\beta$ -ol	W	- 6.1m	203	- 8.1m	204	- 0	183	- 8	- 0	HPdeJ
C31	3 $\beta$ -Chloro-17 $\alpha$ -ethyl-7 $\alpha$ -methyl- oestr-5-en-17 $\beta$ -ol	W	-12.6m	202	-13.3	203	- 0	183	-13	+ 3	HPdeJ
C32	19-Norcholest-5-en-3 $\beta$ -ol (19-norcholesterol)	{S {L			- 6.1	207			- 5	+ 4	
C33	Des-D-13 $\beta$ (H)-androst-5-ene	W			+ 2.8m	202	- 9.2!	185 ( $\lambda_3$ ?)	+ 6	-11	DNK
C34	3 $\beta$ -Chloro-des-D-13 $\beta$ (H)- androst-5-ene	W			- 1.35m	209	+ 2.8m	196 ( $\lambda_2$ ) -16.4! 185 ( $\lambda_3$ )	+ 1	- 8	DNK
C35	Androst-5-ene	W	+ 4.1m	202	+ 5.9	202	-17.2	186	+ 6	-11	DNK
C36	D-Homoandrost-5-ene	W			+ 4.5	201	-13.5	186	+ 6	-11	DNK
C37	Cholest-5-ene	{W {S	+ 2.8	202	+ 3.8m	203	-13.8m	186	+ 6	-11	DNK
C38	Cholest-5-en-2 $\alpha$ -ol	W			+ 4.05m	200	-15.7m	185	+ 6	-11	FS
C39	Cholest-5-en-2 $\beta$ -ol	W			+ 5.5m	202	-12.4m	185	+ 6	-11	FS
C40	Cholest-5-en-3 $\beta$ -ol (cholesterol)	{S {L			+ 1.5	200	- 6.0!	187!	+ 3.5	- 1.5	
C41	Cholest-5-en-3 $\beta$ -ol acetate	W			+ 2.4	195	-10.5!	184!	+ 4.5	- 7.5	DNK
C42	19-Methylcholest-5-en-3 $\beta$ -ol (i.e. with 10 $\beta$ -Et)	W			- 1.2	206	+ 1.95	192 ( $\lambda_2$ ) - 1.9! 185! ( $\lambda_3$ )	+ 0.5	+ 2.5	BAM
C43	Cholest-5-ene-3 $\beta$ ,19-diol 3-acetate	W			+ 7.0	191			?	?	DNK
C44	Cholest-5-ene-3 $\beta$ ,19-diol 3-acetate 19-mesylate	W			- 6.3	200	- 8.5!	185 ( $\lambda_3$ )	?	?	DNK
C45	Cholest-5-en-3 $\alpha$ -ol	W			+ 5.1m	203	-22.1m	185	+ 7.5	-19	DNK
C46	Cholest-5-en-3 $\alpha$ -ol acetate	W			+ 8.1m	197	- 9.0!	184	+10.5	?	DNK
C47	3 $\beta$ -Chlorocholest-5-ene	W			- 2.6	203	+ 1.5 -17.9!	194 183!	+ 1	- 8	JH
C48	3 $\alpha$ -Chlorocholest-5-ene	W			+ 6.9m	197	-14.2	185 ( $\lambda_3$ )	+ 8.5	-16	JH
C49	3 $\beta$ -Fluorocholest-5-ene	W	+ 1.6	199	+ 2.4m	197	-12.1!	184! ( $\lambda_3$ )	+ 2.5	?	JH
C50	3,3-Ethylenedioxycholest-5-ene	{W {L	+ 2.6	199	+ 2.8m	204	-11.9!	184! ( $\lambda_3$ )	(+)	(-)	JH
C51	3 $\beta$ -Methylcholest-5-en-3 $\alpha$ -ol	W	+ 3.95 - 1.4!	203 196	+ 6.9m	200	-16.3m	186	+ 7.5	-19	JH
C52	3 $\alpha$ -Methylcholest-5-en-3 $\beta$ -ol	W	+ 2.0 - 1.6!	201 195!	+ 1.4m	204	-12.9m	186	+ 3.5	- 1.5	JH
C53	4,4-Dimethylcholest-5-ene	W	+ 3.25	200	- 2.2	206	-13.4!	184!	+ 3	?	JH
C54	Androst-5-en-17 $\beta$ -ol	W	+ 1.4m	202					+ 6	-13 <sup>f</sup>	DNK
C55	Androst-5-en-3 $\beta$ -ol	W	+ 2.2!	200!					+ 3.5	- 1.5	DNK
C56	17 $\alpha$ -Methylandrost-5-ene- 3 $\beta$ ,17 $\beta$ -diol	W	+ 1.7m	202					+ 3.5	- 3.5 <sup>f</sup>	DNK
C57	17 $\alpha$ (2'-hydroxyethyl)androst- 5-ene-3 $\beta$ ,17 $\beta$ -diol	W	+ 1.6m	200					+ 3.5	- 3.5 <sup>f</sup>	EAB
C58	3 $\beta$ -(2'-hydroxyethoxy)cholest- 5-ene	W			+ 2.5m	197	- 4.7!	190!	(+)	(-)	JH
C59	25 $R$ -Spirost-5-en-3 $\beta$ -ol (7-enes)	W	+ 2.2!	200!	+ 2.0m	196			+ 3.5	- 1.5	DNK
C60	5 $\alpha$ -Cholest-7-ene	W	- 6.9m	210	- 9.2m	210	0	185	- 8	0	JH
C61	5 $\alpha$ -Cholest-7-en-3 $\beta$ -ol	W	- 6.3m	209	- 7.5m	209			- 8	0	DNK
C62	5 $\alpha$ -Cholest-7-en-3 $\alpha$ -ol	W			- 8.9	209	- 1.7sh	194	- 8	0	DNK
C63	3,3-Dimethoxy-5 $\alpha$ -cholest-7-ene	W	- 7.2m	208					- 8	0	DNK
C64	5 $\alpha$ -Ergost-7-en-3 $\beta$ -ol	S			-11.5	210			- 8	0	DNK
C65	4,4,14 $\alpha$ -Trimethyl-5 $\alpha$ -cholest- 7-ene	W			- 8.8	209	+ 3.4!	187!	- 8	+ 4	JFMCG

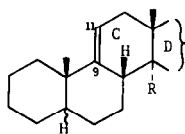


- (c66) R=13 $\alpha$ -H, 13 $\beta$ -<sup>i</sup>Pr  
 (c67) R=13 $\alpha$ -<sup>i</sup>Pr, 13 $\beta$ -H  
 (c68) R=13 $\alpha$ -CH:CH<sub>2</sub>, 13 $\beta$ -Me  
 (c69) R=13 $\alpha$ -Et, 13 $\beta$ -Me



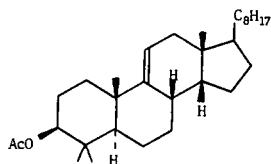
(octant diagrams of similar type to c18)

- (c70) R=13 $\alpha$ -H, 13 $\beta$ -<sup>i</sup>Pr  
 (c71) R=13 $\alpha$ -<sup>i</sup>Pr, 13 $\beta$ -H  
 (c72) R=13 $\alpha$ -CH:CH<sub>2</sub>, 13 $\beta$ -Me  
 (c73) R=13 $\alpha$ -Et, 13 $\beta$ -Me  
 (c74) R=13 $\alpha$ -Et, 13 $\beta$ -Me  
 (with 12 $\beta$ -OH)

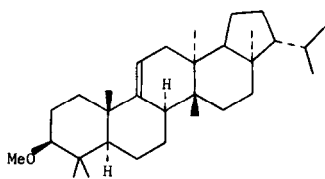


(octant diagram of enantio-c53 type)

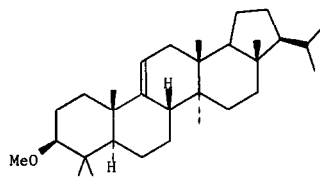
- (c75) R=H (D-homo-5 $\alpha$ -androstan)  
 (c76) R=H (5 $\beta$ -androstan-3 $\alpha$ -ol)  
 (c77) R=H (3 $\alpha$ -OH-5 $\beta$ -cholan-24-oic acid)  
 (c78) R=H (5 $\alpha$ ,25R-spirostan)  
 (c79) R=H (5 $\alpha$ ,25R-spirostan-3 $\beta$ -ol)  
 (c80) R=H (3 $\beta$ -AcO-5 $\alpha$ ,25R-spirostan)  
 (c81) R=Me (4,4-Me<sub>2</sub>-5 $\alpha$ -cholestane)  
 (c82) R=Me (4,4-Me<sub>2</sub>-5 $\alpha$ -cholestan-3 $\beta$ -ol)



(c83)

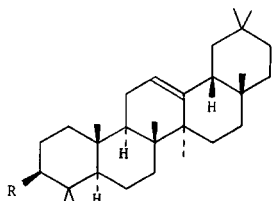


(c84)



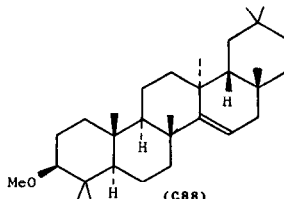
(octant diagram of enantio-c53 type)

(c85)

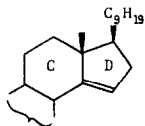


(octant diagram resembles c21)

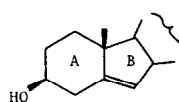
- (c86) R=H  
 (c87) R=AcO



(c88)



(c89)



(c90)

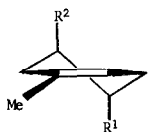
Table 4. (Contd.)

No.	Compound	SOLVENT: Methanol		Hexane (or cyclohexane)		"Calculated"		Source of compound <sup>e</sup>			
		C.d. ref. <sup>a</sup>	$\Delta\epsilon$	$\lambda_1$	$\lambda_2$ and/or $\lambda_3$ <sup>d</sup>	$\Delta\epsilon$	$\Delta\epsilon$ at				
			$\lambda$ (nm)	$\Delta\epsilon$	$\lambda$ (nm)	$\Delta\epsilon$	$\lambda_1$	$\lambda_2$			
C66	13 $\alpha$ (H)-Abiet-7-en-18-oic acid	S		- 5.3	207		- 5	+ 4			
C67	13 $\beta$ (H)-Abiet-7-en-18-oic acid	S		-10.0	205		- 5	+ 4			
C68	Isopimaric acid	W	- 5.3m	207			- 5	+ 4	LJG		
C69	15,16-Dihydroisopimaric acid	W	- 5.5m	210			- 5	+ 4	LJG		
	[8(14)-enes]										
C70	13 $\alpha$ (H)-Abiet-8(14)-en-18-oic acid	S		+ 5.2	209		+ 8	- 2			
C71	13 $\beta$ (H)-Abiet-8(14)-en-18-oic acid	S		+11.2	210		+ 5	- 4			
C72	Sandaracopimaric acid	W	- 5.8!	204!			?	?	LJG		
C73	15,16-Dihydrosandaracopimaric acid	W	+ 5.8m	208			+ 8	- 4	LJG		
C74	12 $\beta$ -Hydroxy-15,16-dihydro-sandaracopimaric acid	W	+ 6.1m	205			+ 8	- 4	LJG		
	[9(11)-enes]										
C75	D-homo-5 $\alpha$ -androst-9(11)-ene	W		+ 8.4	206	- 4.6!	188!	+ 8	- 4	DNK	
C76	5 $\beta$ -Androst-9(11)-en-3 $\alpha$ -ol	(S {L		+11.5	204			+ 8	- 4		
				+11.5	205						
C77	3 $\alpha$ -Hydroxy-5 $\beta$ -chol-9(11)-en-24-oic acid	W	+ 5.4m	209				+ 8	- 4	DNK	
C78	5 $\alpha$ ,25R-Spirost-9(11)-ene	W	+ 8.25m	204	+10.1m	196		+ 8	- 4	JE	
C79	5 $\alpha$ ,25R-Spirost-9(11)-en-3 $\beta$ -ol	W	+ 5.75m	205	+ 7.2m	202	- 2.1!	190!	+ 8	- 4	JE
C80	5 $\alpha$ ,25R-Spirost-9(11)-en-3 $\beta$ -ol acetate	S		+ 9.6	205	- 5.9!	190!	+ 8	- 4		
C81	4,4,14 $\alpha$ -Trimethyl-5 $\alpha$ -cholest-9(11)-ene	W		+14.35m	205			+ 8	- 4	JFMcG	
C82	4,4,14 $\alpha$ -Trimethyl-5 $\alpha$ -cholest-9(11)-en-3 $\beta$ -ol	W	+11.3m	205	+16.5m	202		+ 8	- 4	JFMcG	
C83	4,4-Dimethyl-5 $\alpha$ ,14 $\beta$ -cholest-9(11)-en-3 $\beta$ -ol acetate	W		+11.6	206	- 9.2!	190!	+ 8	- 4	JFMcG	
C84	3 $\beta$ -Methoxyfern-9(11)-ene (arundoin)	W		- 7.9m	208			?	?	SD	
C85	Cylindran (isoarborinol 3-methyl ether)	W		+15.9	202			+ 8	- 4	SD	
	(12-enes)										
C86	Olean-12-ene	W	+ 8.6!	198!	+ 3.0sh ca.202		+11.1!	186!	- 6	+ 7	JH
C87	Olean-12-en-3 $\beta$ -ol acetate ( $\beta$ -amyryn acetate)	W		+ 5.4	199	+13.0!	185!	- 6	+ 7	JH	
	(14-enes)										
C88	Sawamilletin (taraxerol 3-methyl ether)	W		- 7.8m	204	+ 5.9!	188!	?	?	SD	
	(Cyclopentenes)										
C89	5 $\alpha$ -Ergost-14-en-3 $\beta$ -ol	S		- 0.8	210						
C90	B-Norcholest-5-en-3 $\beta$ -ol	W	-19.9m	201	-19.9m	203				SK & F	

<sup>a</sup>See Table 2, footnote <sup>a</sup>. <sup>b</sup>From data in Figures 9 and 10, and Table 6. <sup>c</sup>See Table 2, footnote <sup>c</sup>.

<sup>d</sup>See Table 2, footnote <sup>d</sup>. <sup>e</sup>Ref. 25. <sup>f</sup>Includes allowance for 17 $\beta$ -OH (see text).

tions (*ca.*  $\pm 1$  unit) according to whether R<sup>1</sup> or R<sup>2</sup> is a Me group, respectively. Compounds in this sub-group resemble the analogous *cis*-1,2-disubstituted ethylenes (*trans*- $\Delta^2$ -octalins; 10), the CD band at  $\lambda_2$  similarly being weak or negligible.



(18)



(19)

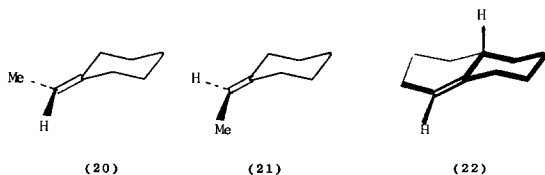
The resemblance at  $\lambda_1$  extends to compounds bearing an " $\alpha$ "-*quasi* equatorial (allylic) substituent at C<sub>trans</sub> (compounds C4, C5 and C9), which show  $\Delta\epsilon$  values only slightly larger than for compounds lacking the allylic substituent. Behaviour at  $\lambda_2$ , however, is quite unlike that of the *cis*-1,2-disubstituted analogues. The observed CD at  $\lambda_2$  is rather weak, although again consignate. The axial allylic Me group in 18 $\alpha$ -urs-20-ene (C8) apparently causes the CD band at  $\lambda_1$  to vanish, while having a large effect at  $\lambda_2$ , but it would be unwise to base general conclusions upon this one compound, which may have a flattened cyclohexene ring.

Tentative conclusions regarding effects of ring chirality and " $\alpha$ " quasi-equatorial groups are as follows (formula 19; *P*-helicity): R = H (no " $\alpha$ " substitution)  $\Delta\epsilon(\lambda_1) + 2.5 \pm 1$ ,  $\Delta\epsilon(\lambda_2)$  very small; R = alkyl:  $\Delta\epsilon(\lambda_1) + 3.5 \pm 1$ ,  $\Delta\epsilon(\lambda_2)$  ca.  $-3$ .

Abiet-13-en-18-oic acid (C6) has a cyclohexene ring with *M*-helicity, like *S*-(-)-limonene (C1). The unique pattern of substitution (equatorial allylic bond at  $C_{gem}$ , and an olefinic isopropyl group) has little effect on the CD behaviour. The cyclopentene derivative (C10), and the bridged ring compounds (C7, C11 and C12) are isolated examples which do not fit into the octalin pattern of structure.

### Group 2

*Exocyclic ethylidene compounds (C13-C17)*. The CD features of the 3-ethylidene  $5\alpha$ -cholestanes (C13 and C14) have been discussed in a recent paper.<sup>25</sup> The main conclusion is that the system (20) and its enantiomer (21)



make large positive and negative contributions to  $\Delta\epsilon$  (ca.  $\pm 6$  to 9 units respectively) in the  $\lambda_1$  region, with larger contributions of opposite sign at  $\lambda_2$ . The configurations assigned by Andersen *et al.*<sup>24</sup> to (*Z*)- and (*E*)-3-ethylidene-1-methylcyclohexanes, from arguments based upon a relationship between CD curves and olefin torsion, agree with our assignments for the 3-ethylidene- $5\alpha$ -cholestanes. The signs of  $\Delta\epsilon$  for the 17 $\alpha$ -ethylidene D-homoandrosterone (C17) suggest that it is the (*E*)-(*trans*) isomer, although this has not been established unambiguously. It was prepared from the 17 $\alpha$ -ketone by the action of ethylenetriphenylphosphorane, and appeared to be the sole product.<sup>41</sup>

The pregn-17(20)-enes (C15 and C16) give signs in the opposite sense to those expected from a simple comparison of the chiral ethylenecyclopentane unit with the ethylenecyclohexanes (20 and 21). The effect of ring size, and the roles of the 13 $\beta$ -Me group and ring C, cannot be assessed from present data.

### Group 3

" $\Delta^{1(9)}$ -Octalin" types (C18-C88). Oestr-4-ene and 5-ene derivatives show that a " $\Delta^{1(9)}$ -octalin" in the configuration and conformation (22) contributes about +5 to  $\Delta\epsilon$  at  $\lambda_1$ , and makes a contribution of similar size but opposite sign at  $\lambda_2$ .<sup>25</sup> [The apparent discrepancy between  $\Delta\epsilon$  values for oestr-4-ene (C18) and oestr-5-en-17 $\beta$ -ol (C25) at  $\lambda_2$  is probably due to a  $\Delta\epsilon$  contribution of ca.  $-2$  units from the secondary 17 $\beta$ -OH group at 191 nm;<sup>45</sup> compare C18 and C19.]

We have already shown<sup>25</sup> that the sign and a large part of the magnitude of  $\Delta\epsilon$  for the " $\Delta^{1(9)}$ -octalin" unit derives from the contribution of the fragment of structure corresponding to an ethylenecyclohexane (22; heavy lines) and that much of the observed CD of oestr-4-enes and 5-enes, as well as of steroidal 7-enes and 9(11)-enes, can be attributed to that part of their structure which corresponds to the bicyclic " $\Delta^{1(9)}$ -octalin" fragment, either as 22, or as its enantiomer.

Our present objective is therefore to clarify the contributions of additional structural features, and in particular those which can be regarded as allylic substituents at  $C_{gem}$ ,  $C_{trans}$  or  $C_{cis}$  (Fig. 9).

The effects of alkyl substitution at each of the three allylic centres are considered separately (allylic heteroatom substitution will be discussed elsewhere).

*Allylic alkyl substituents*. Substitution at  $C_{trans}$  is limited to 10 $\beta$ -methyl and its derivatives, including 10 $\beta$ -Et (C42), in steroidal 4-enes and 5-enes. A 10 $\beta$ -Me substituent lowers the wavelength  $\lambda_1$  from about 207–210 nm to about 200–202 nm, an average shift of ca. 8 nm. This blue-shift is accompanied by a large dissignate effect of the 10 $\beta$ -Me substituent on  $\Delta\epsilon$ , averaging 12–13 units in the 4-enes and ca. 10 units in the 5-enes. 10 $\beta$ -Et has smaller effects on  $\lambda_1$  and on  $\Delta\epsilon$ , but each shift is in the same sense as for 10 $\beta$ -Me. The effects of  $C_{trans}$ -alkyl on  $\lambda_2$  are less clearly defined, but 10 $\beta$ -Me appears to cause a blue-shift in  $\lambda_2$ , accompanied in this case by a large consignate contribution to  $\Delta\epsilon$  (ca. 10–16 units). Again, the effect of 10 $\beta$ -Et is smaller but otherwise similar. There is no certainty, however, that the CD curves obtained in the region below 195 nm are sufficiently reliable to permit assignment of the CD maxima listed under  $\lambda_2$  (Table 3) to only a single transition. Any apparent correlations here must be regarded as only tentative.

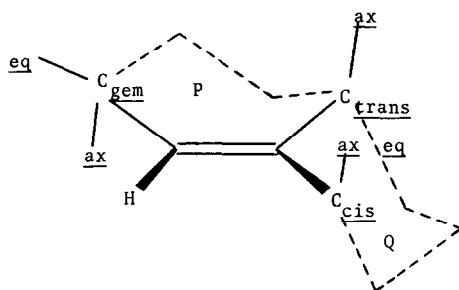
There are very few examples of  $C_{gem}$ -substitution. Compound C24 (3 $\alpha$ -CF<sub>3</sub>- $\Delta^4$ ) shows little effect of the trifluoromethyl group on  $\Delta\epsilon$ , but there is a large blue-shift in  $\lambda_1$ . A 7 $\alpha$ -Me substituent in  $\Delta^5$ -compounds (C30 and C31) makes a moderate negative contribution to  $\Delta\epsilon$  at  $\lambda_1$  (ca.  $-3$ ; consignate), and causes a small blue-shift.

Substitution at  $C_{cis}$  is even less common. The only example available for comparison with its parent olefin is a 14 $\alpha$ -methyl- $\Delta^7$  steroid (C65), where there is no clear effect attributable to 14 $\alpha$ -Me.

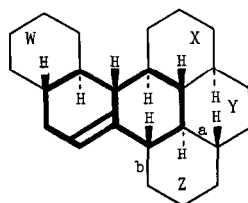
The conclusions for this group of compounds are summarised in Fig. 9.

*Effects of "third" rings (Fig. 10)*. Since the magnitudes of  $\Delta\epsilon$  are quite similar for  $\Delta^4$ - and  $\Delta^5$ -unsaturated steroids, the third ring appears to make little CD contribution in either structure. The situation is quite different for 7-enes and 9(11)-enes. Although these compounds show signs of CD curves dominated by the absolute configuration of the octalin unit which comprises rings B and C, they also exhibit enhanced magnitudes of  $\Delta\epsilon$  compared with  $\Delta^4$ - and  $\Delta^5$ -unsaturated steroids. We attribute the extra contributions tentatively to the additional rings (ring D in  $\Delta^7$ -compounds; ring A in  $\Delta^{9(11)}$ -compounds).

Possible locations of a third ring on the two rings of a "1(9)-octalin" unit are illustrated in Fig. 10, which represents a composite structure including the "third" rings found in  $\Delta^4$ ,  $\Delta^5$ ,  $\Delta^7$  and  $\Delta^{9(11)}$ -unsaturated compounds (or their enantiomers). The individual rings W (*ent*- $\Delta^5$ ) and X( $\Delta^4$ ) make little or no contribution at either  $\lambda_1$  or  $\lambda_2$ . Ring Y makes a small contribution (ca. +1.5) at  $\lambda_1$  (see compound C20) but has no clear effect at  $\lambda_2$ . Ring Z (*ent*- $\Delta^7$ ) is more important, and contributes an estimated  $+3 \pm 1$  units to  $\Delta\epsilon$  at  $\lambda_1$ . A very similar value (sign reversed) is estimated from  $\Delta^{9(11)}$  steroids, suggesting that the size of the third ring Z is relatively unimportant, and that the 10 $\beta$ -Me group ( $C_{cis}$ -axial) is also without significant effect, as concluded above. The effect of ring Z at  $\lambda_2$  is less clear, but most compounds of this type exhibit no distinct maximum in the region 190–194 nm, suggesting that ring Z nullifies the contribution of the " $\Delta^{1(9)}$ -octalin" component.



Structural type	$\delta\Delta\epsilon$ values	
	$\lambda_1$	$\lambda_2$
(i) 1-Methyl-cyclohexene (Ring P only; $C_{cis} = \text{Me}$ )	+2.5	ca.0
<u>Substituent:-</u>		
<u>eq</u> -Me at $C_{trans}$	+ 1 (dissignate)	- 3 (consignate)
(ii) Ethylidenecyclohexane (Ring Q only; $C_{gem} = \text{Me}$ )	+7	-9
(iii) $\Delta^{1(9)}$ -Octalin (Rings P + Q)	+5	-4
<u>Substituents:-</u>		
<u>ax</u> -Me at $C_{trans}$	-11 (dissignate)	+15 (consignate)
<u>ax</u> -Et at $C_{trans}$	- 8 (dissignate)	+11 (consignate)
<u>ax</u> -Me at $C_{gem}$	+ 3 (consignate)	+ 2 (consignate)
<u>ax</u> -Me at $C_{cis}$	ca.0	- 4 (consignate)

Fig. 9. Substitution patterns for trisubstituted-ethylene analogues, and their  $\delta\Delta\epsilon$  values.

Ring Label	Steroid Type	$\delta\Delta\epsilon$ at $\lambda_1$	$\delta\Delta\epsilon$ at $\lambda_2$
W	Ring C in ( <i>ent</i> ) $\Delta^5$ -steroid	ca.0	ca.0
X	Ring C in $\Delta^4$ -steroid	ca.0	ca.0
Y	Ring B in "pentacyclic" steroid derivative (C20)	+1.5	small
Z	Ring A in $\Delta^{9(11)}$ -steroid, or ring D in ( <i>ent</i> ) $\Delta^7$ -steroid*	+3	+4

\*The difference in size of ring D seems unimportant.

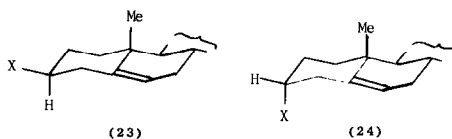
Fig. 10. Contributions of "third" rings to CD of extended  $\Delta^{1(9)}$ -octalin derivatives.

It seems probable that the Z-ring effect can be regarded essentially as a combination of two smaller increments, one due to the homoallylic bond (a), also present in ring Y, and the other due to the equatorial allylic bond (b). It would be unwise, however, to try to separate these contributions with the limited data available, so the entire rings will be treated for the present as the most convenient structural units.

*Miscellaneous compounds of Class 3.* A few compounds in Table 3 which do not have an "all-trans" "all-chair" structure would not be expected to fit the general pattern. These are compounds C84, C86, C87 and C88, and the cyclopentene analogues C89 and C90, for which no conclusions are possible at present. The main value of the data will be for comparisons with new compounds of analogous structures.

**Homoallylic ("β") electronegative substituents.** A full report on a wide range of alkenes substituted in homoallylic positions will be presented later. For the present we report only the effects of some of the more common homoallylic electronegative substituents on the CD behaviour of steroidal 4-enes and 5-enes.

Compounds of the 3-substituted  $\Delta^5$ -type (Table 4) provide values of substituent effects ( $\delta\Delta\epsilon$ ) which are listed in Table 6. A clear pattern is evident for  $\delta\Delta\epsilon$  values at  $\lambda_1$ , where each equatorial substituent (23) provides a consignate contribution which is accompanied by a blue-shift of  $\lambda_1$ . Axial substituents (24) give dissignate contributions and have little effect on  $\lambda_1$ . The tabulated effects at  $\lambda_2$  are less clearly supported by the data, in view



of uncertainties as to assignments of CD bands in this region, but the contributions associated with particular functional groups are generally of opposite sign to those observed at  $\lambda_1$ .

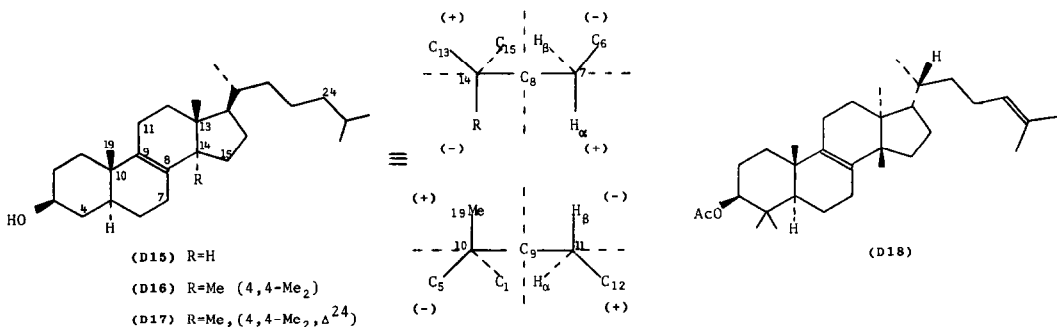
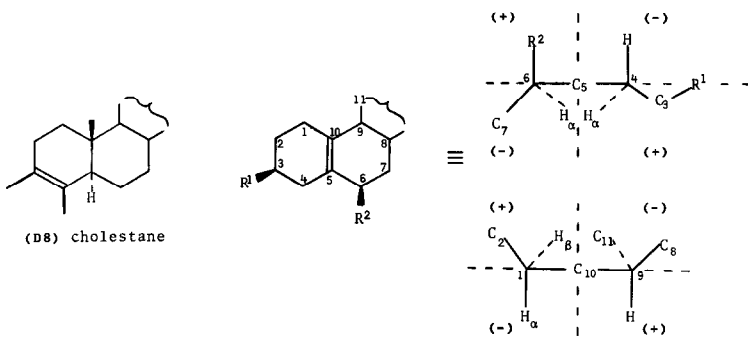
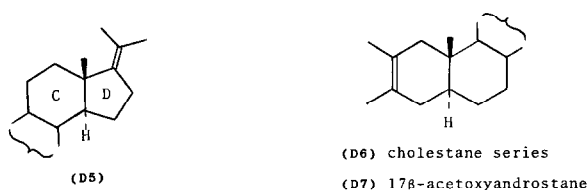
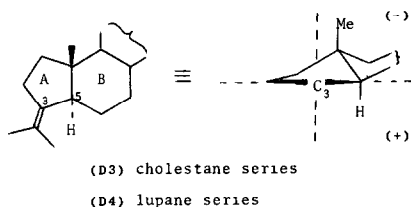
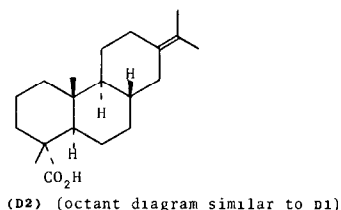
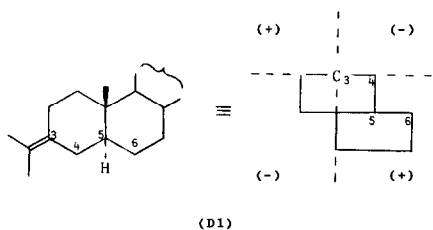
#### Class D

**Tetrasubstituted ethylenes (Table 5).** Previous analyses of CD data for tetrasubstituted olefins have ignored

Formulae of Compounds (see Table 5 for names and CD data).

Octant diagrams give the view from the mid-point of the C=C bond.

Signs indicated for octants are those which would correspond to *consignate* behaviour (right-handed "Octant Rule").





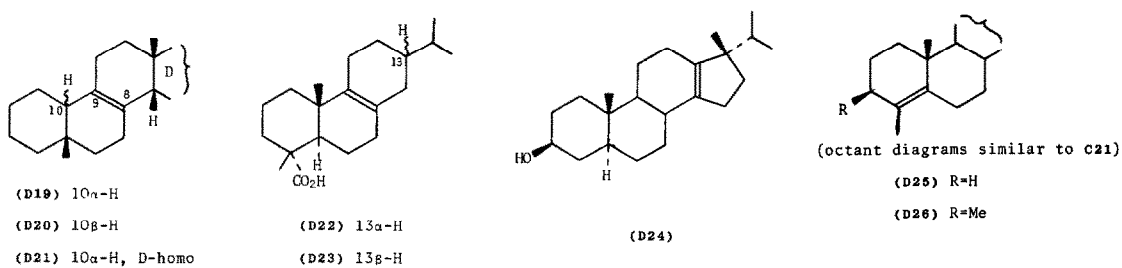


Table 5. CD data for tetrasubstituted ethylenes

No.	Compound	SOLVENT: Methanol		Hexane (or cyclohexane)		"Calculated"		Source of compounds <sup>a</sup>		
		C.d. ref. <sup>a</sup>	$\Delta\epsilon$	$\lambda_0$	$\lambda_1$ and $\lambda_2$ <sup>d</sup>	$\Delta\epsilon^b$ at $\lambda_1$	$\lambda_2$			
<u>Isopropylidene cycloalkanes</u>										
D1	3-Isopropylidene-5 $\alpha$ -cholestane	W F & S		+ 0.3	225	+ 2.5 (+)	209 209	+0.3 +2.5	RJM	
D2	Abiet-13(15)-en-18-oic acid	S				+ 1.7	208	+0.3 +2.5		
D3	3-Isopropylidene-A-nor-5 $\alpha$ -cholestane	W				{ + 8.4 { - 5.8!	209 ( $\lambda_1$ ) 185! ( $\lambda_2$ )	? ?	JL	
D4	3-Isopropylidene-A-nor compound in lupane series (' $\gamma$ -lupene')	W				{ + 3.3 { - 5.8!	208 ( $\lambda_1$ ) 195! ( $\lambda_2$ )	? ?	TGH	
D5	17-Isopropylidene-5 $\alpha$ -androstane	F & S				+ 4.9	193 ( $\lambda_2$ ?)	? ?		
<u>'1,2-Dimethylcyclohexenes'</u>										
D6	2,3-Dimethyl-5 $\alpha$ -cholest-2-ene	W		- 0.3	224	+ 8.6	198	-0.4 + 8	JH	
D7	2,3-Dimethyl-5 $\alpha$ -cholest-2-en-17 $\beta$ -ol 17-acetate	W		- 0.4	221	+ 8.2	196	-0.4 + 8	DNK	
D8	3,4-Dimethyl-5 $\alpha$ -cholest-3-ene	W		+ 0.7	222	-11.1	199	+0.4 -15	JL	
<u>'<math>\Delta^9</math>-Octalins'</u>										
D9	Oestr-5(10)-en-17 $\beta$ -ol	W	+ 7.75	200		+ 7.7	198	0.0 + 7	HPdeJ	
D10	17 $\alpha$ -Ethyl-oestr-5(10)-en-17 $\beta$ -ol	W	+ 8.3!	200!		+ 7.7	201	0.0 + 7	HPdeJ	
D11	Oestr-5(10)-ene-3 $\beta$ ,17 $\beta$ -diol	S L				+ 7.6 + 7.7	200 200	0.0 + 7		
D12	6 $\beta$ -Methyl-oestr-5(10)-ene-3 $\beta$ ,17 $\beta$ -diol diacetate	W		- 0.5	218	ca.0	195-185	-2 + 4	DNK	
D13	6 $\beta$ -Methyl-19-norcholest-5(10)-en-3 $\beta$ -ol	W	- 1.15	217	- 0.3	217	+ 2.7	ca.200	-2 + 4	MK
D14	6 $\beta$ -Hydroxymethyl-19-norcholest-5(10)-en-3 $\beta$ -ol	W	- 2.3 + 3.6	216 199				-2 + 4	MK	
D15	5 $\alpha$ -Cholest-8-en-3 $\beta$ -ol	W	- 2.9	223	- 3.1	219	+ 1.2	203	-2 <sup>e</sup> - 3 <sup>e</sup>	JH
D16	Lanost-8-en-3 $\beta$ -ol	W S	+ 3.8	205			+ 3.9 + 3.2 - 4.2!	206 205 ( $\lambda_1$ ) 187! ( $\lambda_2$ )	0.0 <sup>e</sup> 0.0 <sup>e</sup>	JFMcG
D17	Lanosta-8,24-dien-3 $\beta$ -ol (lanosterol)	S L W					+ 2.0 + 2.2 + 5.4 - 1.9!	205 205 205 ( $\lambda_1$ ) 185! ( $\lambda_2$ )	0.0 <sup>e</sup> 0.0 <sup>e</sup>	
D18	3 $\beta$ -Acetoxy-euph-8-ene (euphyl acetate)	W	- 3.0	211	- 3.1	211	+ 2.1 + 4.0!	194 187!	(-) (+)	TGH
D19	5-Methyl-19-nor-5 $\beta$ ,10 $\alpha$ ,14 $\beta$ -androst-8-ene	W		- 2.7	216				0.0 <sup>e</sup>	PMS
D20	5-Methyl-19-nor-5 $\beta$ ,14 $\beta$ -androst-8-ene	W		- 2.1 - 2.0	212 208				0.0 <sup>e</sup> +10 <sup>e</sup>	PMS
D21	5-Methyl-D-homo-19-nor-5 $\beta$ ,10 $\alpha$ ,14 $\beta$ -androst-8-ene	W		- 1.5	213	+ 2.0	191			PMS
D22	13 $\alpha$ (H)-Abiet-8-en-18-oic acid	S				+ 8.0	199	-3 (+)		
D23	Abiet-8-en-18-oic acid	S				- 2.2	215	-2 + 5		
D24	17 $\beta$ -Methyl-17 $\alpha$ -isopropyl-18-nor-5 $\alpha$ -androst-13-en-3 $\beta$ -ol	W	- 1.8	211	- 0.9	204( $\lambda_0$ ?)	+ 1.1 - 3.7	196 ( $\lambda_1$ ) 185! ( $\lambda_2$ )		IS
<u>'<math>\Delta^1(9)</math>-Octalins'</u>										
D25	4-Methylandrost-4-ene	W		- 3.9	217	+ 7.8	197	-4 + 8	TGH	
D26	3 $\beta$ ,4-Dimethylcholest-4-ene	W				+20.6	197	-4 +15	JL	
D27	6-Methyl-oestr-5-ene-3 $\beta$ ,17 $\beta$ -diol diacetate	W						+2 <sup>f</sup> -11 <sup>f</sup>	DNK	

Table 5. (Contd.)

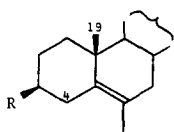
No.	Compound	SOLVENT: Methanol			Hexane (or cyclohexane)				"Calculated"		Source of compounds <sup>e</sup>
		C.d. ref. <sup>a</sup>	$\Delta\epsilon$	$\lambda$ (nm)	$\Delta\epsilon$	$\lambda_0$ $\lambda$ (nm)	$\lambda_1$ and $\lambda_2$ <sup>d</sup> $\Delta\epsilon$	$\lambda$ (nm)	$\Delta\epsilon^b$ at $\lambda_1$	$\lambda_2$	
D28	6-Methylcholest-5-ene	W			+ 5.9	218	-14.6	190	+4	- 8	DNK
D29	6-Methylcholest-5-en-3 $\beta$ -ol	W	+ 2.3 - 4.1!	215 200!	+ 2.7	216	- 8.6!	185!	+4 <sup>f</sup>	- 8 <sup>f</sup>	DNK
D30	6-Methylcholest-5-en-3 $\beta$ -ol 3-acetate	W			+ 3.6	214	-14.5	192	+4 <sup>f</sup>	- 8 <sup>f</sup>	DNK
D31	6-Methylandro-5-en-3 $\beta$ -ol	W	+ 3.3 - 5.7	216 195					+4 <sup>f</sup>	- 8 <sup>f</sup>	PT
D32	4,4,6-Trimethylcholest-5-en- 3 $\beta$ -ol	W			weakly (+)	213-220	- 9.0	199	+2 <sup>f</sup>	-11 <sup>f</sup>	JSEH
D33	3 $\beta$ -Chloro-6-methylcholest-5-ene	W			+ 6.9	213	-20.0	190	+4 <sup>f</sup>	- 8 <sup>f</sup>	DNK
D34	6-Methyl-25R-spirost-5-en-3 $\beta$ -ol 3-acetate	W	+ 2.5 - 7.9!	212 198!	+ 1.7	214	-16.6!	192!	+4 <sup>f</sup>	- 8 <sup>f</sup>	DNK
D35	6-Methylpregn-5-ene-3 $\beta$ ,20 $\beta$ - diol	W	+ 2.6 - 4.3	218 202					+4 <sup>f</sup>	- 8 <sup>f</sup>	DNK
D36	4,4-Dimethyl-1(10 $\rightarrow$ 5 $\alpha$ ) <i>abeo</i> - cholest-9-ene-3 $\beta$ ,6 $\alpha$ -diol	W	+ 5.05 - 6.0!	221 201!					+4	-15	DNK
D37	11-Methyl-5 $\alpha$ ,25R-spirost- 9(11)-ene	W	+10.4!	203!			+11.0	200	0	+14	JE
D38	11-Methyl-5 $\alpha$ ,25R-spirost- 9(11)-en-3 $\beta$ -ol	W	+ 9.4!	200!			+12.1!	195!	0	+14	JE
D39	11-Methyl-5 $\alpha$ ,25R-spirost- 9(11)-en-3 $\beta$ -ol 3-acetate	W	+ 6.9!	200!			+ 8.3	195	0	+14	JE
D40	C-Nor-D-homo-5 $\alpha$ ,25R-spirost- 13(17 $\alpha$ )-en-3 $\beta$ -ol	W	- 6.25	209	- 8.6	208	+ 5.6!	195!	(-)	(+)	DNK
D41	C-Nor-D-homo-5 $\alpha$ ,25R-spirost- 13(17 $\alpha$ )-en-3 $\beta$ -ol 3-acetate	S			-12.3	210	+16.6!	187!	(-)	(+)	DNK
<u>Doubly-exocyclic olefins</u>											
D42	5 $\alpha$ -Cholest-8(14)-ene	W	- 3.9 + 3.4!	223 203!	- 5.1	221	+ 4.4	203	-2.5	+ 5	JH
D43	5 $\alpha$ -Ergost-8(14)-en-3 $\beta$ -ol	S			- 7.8	221	+ 5.85	202	-2.5	+ 5	
D44	5 $\alpha$ -Ergost-8(14)-en-3 $\beta$ -ol 3-acetate	S			- 9.1	221	+ 8.2	202	-2.5	+ 5	
D45	Methyl-3 $\beta$ -acetoxy-5 $\beta$ -eta- 8(14)-enate	S			- 2.4	221	+ 3.0	206	-2.5	+ 5	
<u>Derivatives of 5-methyl-19-nor-5<math>\beta</math>-cholest-9-ene (Westphalen series)</u>											
D46	3 $\beta$ -OH	W	+ 1.2 - 5.15	220 199			- 5.5 + 7.1!	199 ( $\lambda_1$ ) 185! ( $\lambda_2$ )	+0.5	-15	JH
D47	3 $\beta$ ,6 $\beta$ -(OH) <sub>2</sub>	W	+ 7.8!	200!	- 0.7	220	+ 7.5sh +11.6!	200 ( $\lambda_1$ ) 188! ( $\lambda_2$ )	-2.5	+11	DNK
D48	3 $\beta$ ,6 $\beta$ -(OAc) <sub>2</sub>	W	+ 9.9!	203!			+10.6!	200! ( $\lambda_1$ )	-2.5	+11	DNK
D49	3 $\beta$ -OAc,6 $\beta$ -OMe	W	+ 2.8!	200!							DNK
D50	3 $\beta$ -OAc,6 $\beta$ -F	W	+10.0!	199!			+ 4.1sh +13.4!	202 ( $\lambda_1$ ) 190! ( $\lambda_2$ )	-2.5	+11	DNK
D51	3 $\beta$ -OAc,6 $\beta$ -Cl	W					+26.1	190 ( $\lambda_1$ )	-2.5	+11	DNK
D52	3 $\beta$ -OAc,6 $\beta$ -Br	W	+11.2!	197!					-2.5	+11	DNK
D53	3 $\alpha$ -Cl,6 $\beta$ -OAc	W					+12.0	193 ( $\lambda_1$ )	-2.5	+11	DNK
D54	$\Delta^{13(18)}$ -unsaturated rearrangement product from $\gamma$ -lupene	W			+ 4.4	220	- 6.1	199 ( $\lambda_1$ )	?	?	TGH
<u>Cyclopentenes</u>											
D55	" <i>iso</i> - $\gamma$ -Lupene"	W			+ 3.3	208	- 5.8!	195! ( $\lambda_1$ )			TGH
D56	5,14-Dimethyl-18,19-bisnor- 5 $\beta$ ,14 $\beta$ ,20 $\beta$ -cholest-13(17)-ene	W			- 7.1	211					PMS
D57	5,14-Dimethyl-18,19-bisnor- 5 $\beta$ ,14 $\beta$ ,20R-cholest-13(17)-ene	W			- 9.55	211					PMS
D58	4,4,5,14-Tetramethyl-18,19- bisnor-5 $\beta$ ,14 $\beta$ -cholest-13(17)- ene-3 $\beta$ ,6 $\alpha$ -diol 3-acetate	W	- 7.5	210							DNK
D59	Isceuphenyl acetate	W			+ 2.5	210	- 3.9!	194)			TGH

<sup>a</sup>See Table 2, footnote <sup>a</sup>. <sup>b</sup>From data in Figure 11. <sup>c</sup>See Table 2, footnote <sup>c</sup>. <sup>d</sup>See Table 2, footnote <sup>d</sup>.

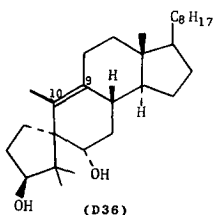
<sup>e</sup>"Calculated" values ignore the five-membered nature of ring D: see text.

<sup>f</sup>Including no allowance

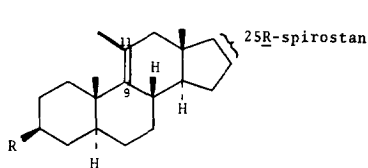
for 3 $\beta$ -substituent. <sup>g</sup>See Table 2, footnote <sup>e</sup>.



- (D27) R=OAc, 19-nor (17 $\beta$ -acetoxy-oestrane)
- (D28) R=H (cholestane)
- (D29) R=OH (cholestane)
- (D30) R=OAc (cholestane)
- (D31) R=OH (androstane)
- (D32) R=OH (4,4-Me<sub>2</sub>-cholestane)
- (D33) R=Cl (cholestane)
- (D34) R=OAc (25R-spirostan)
- (D35) R=OH (pregnan-20 $\beta$ -ol)

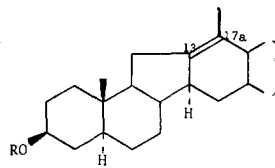


(D36)  
(octant diagram of enantio-c18 type)

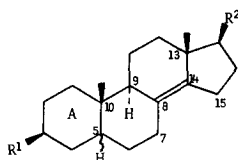


- (D37) R=H
- (D38) R=OH
- (D39) R=OAc

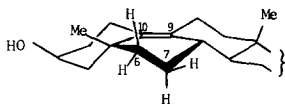
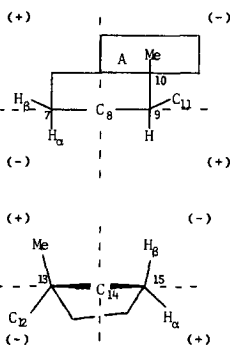
(octant diagram of enantio-c53 type)



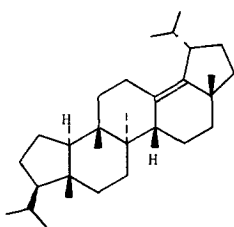
- (D40) R=OH
- (D41) R=OAc



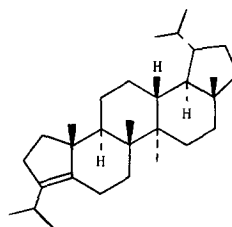
- (D42) R<sup>1</sup>=H, R<sup>2</sup>=C<sub>8</sub>H<sub>17</sub>, 5 $\alpha$ -H
- (D43) R<sup>1</sup>=OH, R<sup>2</sup>=C<sub>9</sub>H<sub>19</sub>, 5 $\alpha$ -H
- (D44) R<sup>1</sup>=OAc, R<sup>2</sup>=C<sub>9</sub>H<sub>19</sub>, 5 $\alpha$ -H
- (D45) R<sup>1</sup>=OAc, R<sup>2</sup>=COOEt, 5 $\beta$ -H



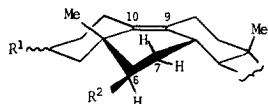
(D46) Ring B has M-helicity



(D54)

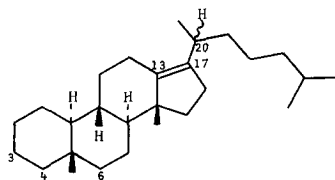


(D55)



Ring B has P-helicity

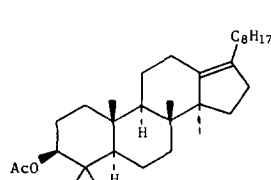
- (D47) R<sup>1</sup>=R<sup>2</sup>= $\beta$ -OH
- (D48) R<sup>1</sup>=R<sup>2</sup>= $\beta$ -OAc
- (D49) R<sup>1</sup>= $\beta$ -OAc, R<sup>2</sup>=OMe
- (D50) R<sup>1</sup>= $\beta$ -OAc, R<sup>2</sup>=F
- (D51) R<sup>1</sup>= $\beta$ -OAc, R<sup>2</sup>=Cl
- (D52) R<sup>1</sup>= $\beta$ -OAc, R<sup>2</sup>=Br
- (D53) R<sup>1</sup>= $\alpha$ -Cl, R<sup>2</sup>=OAc



(D56) 20S

(D57) 20R

(D58) 20R (3 $\beta$ -OAc, 4,4-Me<sub>2</sub>,6 $\alpha$ -OH)



(D59)

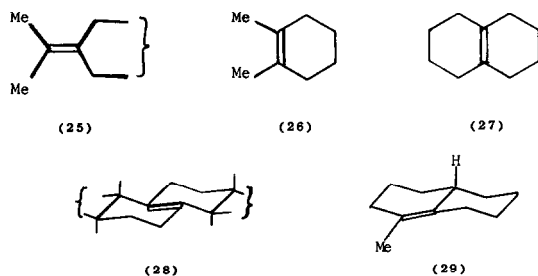
differences in wavelength of the *first observed* CD band, which has appeared anywhere between about 221 nm [steroidal 8(14)-enes] and 200 nm [19-nor-steroidal 5(10)-enes]. We have based the present analysis on the postulate (p. 2478) that  $\lambda_1$  is usually in the region of  $202 \pm 8$  nm, and that an additional low-energy transition sometimes gives rise to an additional CD band at  $220 \pm 5$  nm, which we designate as  $\lambda_0$  in view of its unusual character. Analysis of  $\Delta\epsilon$  values in each of these wavelength regions has revealed some reasonable regularities, especially at  $\lambda_0$ . Where no CD band was detected, either in the  $\lambda_0$  or in the  $\lambda_1$  region, a zero value of  $\Delta\epsilon$  has been assumed. UV spectra of a few selected olefins in this group all showed long-wavelength (215–225 nm) shoulders on the stronger absorption band in the  $\lambda_1$  region, and curve-resolution gave acceptable Gaussian components of the UV spectra in the  $\lambda_0$  region (near 220 nm). Structural contributions ( $\delta\Delta\epsilon$ ) derived from study of CD curves and considered to be the best available at present, are based upon the considerations which follow.

### Group 1

**Isopropylidene compounds (D1–D5).** Compounds of the isopropylidene-cycloalkane type (25) all exhibit a strong CD band at  $\lambda_1$ . The only compound available for more careful study [3-isopropylidene-5 $\alpha$ -cholestane (D1)] also gave a very weak CD band at 225 nm ( $\lambda_0$ ). The signs of  $\Delta\epsilon$  at both  $\lambda_0$  and  $\lambda_1$  correspond to that found at  $\lambda_1$  for the corresponding 3-methylene compound (A13). The sign of  $\Delta\epsilon$  at  $\lambda_1$  for all the compounds in the group is also the same as that found in analogous exocyclic methylene compounds: for isopropylidene-decalins (D1, D2) the sign suggests consignate behaviour of the " $\beta$ "-equatorial bond of the second ring. The sign of  $\Delta\epsilon$  for the isopropylidene-cyclopentanes may possibly reflect the sense of twist of the 5-membered ring, but data are insufficient for a proper analysis. The reported wavelength (193 nm) of the CD maximum for 17-isopropylidene-5 $\alpha$ -androstanone (D5) suggests comparison with the lowest observed CD band ( $\lambda_2$ ?) in compounds D3 and D4, rather than with the  $\lambda_1$  band at 208–209 nm.

### Group 2

**1,2-Dimethylcyclohexenes (D6–D8).** The very weak CD band at  $\lambda_0$  has a sign opposite to that observed at  $\lambda_1$  for analogous olefins of Classes B or C, which lack both or one of the substituent methyl groups respectively. The sign is presumably related to the conformation of the cyclohexene ring in the *opposite* sense to that indicated in Fig. 7 (positive CD for *M*-helicity, negative CD for *P*-helicity). The sign of the CD band at  $\lambda_1$  for compounds (D6–D8), however, matches that for corresponding olefins of Classes B or C, although the wavelength  $\lambda_1$  is unexpectedly blue-shifted for the tetrasubstituted olefins.



The 1,2-dimethylcyclohexene fragment (26) is seen as a key component of the structures discussed in the following sections, and the characteristic  $\Delta\epsilon$  values at  $\lambda_0$  and  $\lambda_1$  for compounds D6 and D7 appear to be applicable in other situations where similar fragments occur.

### Group 3

**" $\Delta^{9(10)}$ -Octalins" (27).** (D9–D23; cf. also D24). Consideration of the data listed under  $\lambda_0$  suggests that a significant CD band appears in this region only when at least one " $\alpha$ "-axial (allylic) Me group is present. This seems reasonable in that the " $\Delta^{9(10)}$ -octalin" fragment (27) can be regarded as comprising two overlapping units, each of type 26, with the olefinic bond and its four attached C atoms shared by the two rings. Moreover in most compounds of this type the two rings are of opposite chirality (i.e. the  $\pi$ -orbital defines a symmetry plane of the octalin component), so that little if any chiroptical behaviour would be expected from the bicyclic system alone. " $\alpha$ "-Axial alkyl substitution introduces a dissignate contribution of magnitude averaging  $\pm 2$  units at  $\lambda_0$ . The CD band ( $\lambda_0$ ) then appears at a rather short wavelength, between 211 and 219 nm, depending upon the number of such substituent groups.

The generally stronger CD band at  $\lambda_1$  appears to be dominated by a dissignate contribution of any " $\alpha$ "-equatorial bond [e.g. the 9(11)-bond in 5(10)-enes]. The corresponding allylic bonds in an 8-ene (28) [C(10)-C(1) and C(14)-C(15)] appear to have mutually compensating effects, resulting from their locations in octants of opposite signs. The different sizes of rings A and D, however, probably cause subtle differences of geometry and strain between the two "ends" of the 8-ene molecule, leaving a residual positive CD in the 14 $\alpha$ -methyl-8-enes (D16 and D17), where the other main features are internally compensated by symmetry. A similar deviation due to the size of ring D is apparent in the ordinary 8-ene (D15) (see also " $\beta$ "-equatorial effects, below).

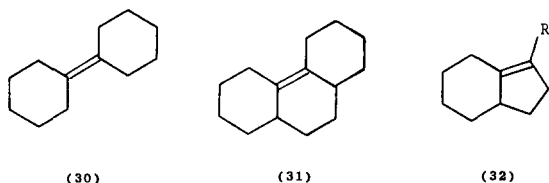
An " $\alpha$ "-axial Me group makes its own weakly dissignate contribution to  $\Delta\epsilon$  at  $\lambda_1$ , as at  $\lambda_0$  (compare, for example, D15, and D16, which reveal the effect of 14 $\alpha$ -Me;  $\delta\Delta\epsilon$  ca. +2.5).

### Group 4

**1-Methyl-" $\Delta^{10(9)}$ -octalins" (D25–D39).** The 1-methyl-" $\Delta^{10(9)}$ -octalin" unit itself (29) probably makes a contribution (2 units) at  $\lambda_0$  of sign following that of a "1,2-dimethylcyclohexene" with the same sense of twist of the unsaturated ring (see above). The other major part of the observed CD at  $\lambda_0$  corresponds to dissignate effects (ca. 2 units) of " $\alpha$ "-axial Me substituents [contrast D27 and D28–D30, with allowance for probable small consignate (negative) effects of 3 $\beta$ -substituents: cf. p. 2498]. Values of  $\Delta\epsilon$  at  $\lambda_1$  are generally large, and have signs opposite to those at  $\lambda_0$ . The C-nor-D-homo olefins (D40, D41) follow a similar pattern, although their structure is not strictly of " $\Delta^{10(9)}$ -octalin" type. 11-Methyl-9(11)-enes behave like 19-norsteroidal 4-enes with an extra " $\alpha$ "-axial (10 $\beta$ ) Me group, indicating that only the bicyclic environment of the olefinic bond is important.

### Group 5

**Doubly-exocyclic olefins (D42–D54).** Compounds which include within their structures a symmetrical bicyclohexylidene unit (30) [e.g. 9(10)-unsaturated 19-norsteroids of the "Westphalen" series; D46 to D54] should exhibit CD only by virtue of the presence of additional



structural features [e.g. the twisted "middle" ring of tricyclic structures (31), and the 6 $\beta$ -substituent and 5 $\beta$ -Me group in the "Westphalen" series]. The signs, though not necessarily the magnitudes of  $\Delta\epsilon$ , for this group of compounds are reproduced by appropriate summation of the contributions (Fig. 11) of structural features discussed in the foregoing paragraphs (see "calculated" values of  $\Delta\epsilon$  in Table 5). The available data are insufficient to provide reliable magnitudes of  $\delta\Delta\epsilon$  for any further contributing features. No allowance has been introduced for the presence of a 5-membered ring in compounds **D42-D45** and **D54**, or for C(6) substituents in the "Westphalen" series of compounds, except insofar as these are known to control the conformation of ring B.<sup>46</sup> Homoallylic (" $\beta$ ") substitution has also been ignored. The correspondence between "predicted" and observed  $\Delta\epsilon$  values is gratifying in view of these omissions.

#### Group 6

*Cyclopentenenes (D55-D59)*. The bicyclic environment (32) of the olefinic bond in the  $\Delta^{13(17)}$ -olefins of the cholestane series (**D56-D58**) resembles that in  $\Delta^{10(9)}$ -octalins (**29**), except in regard to ring size; the sign of  $\Delta\epsilon$  at  $\lambda_0$  is the same for compounds of the same absolute configuration, although the magnitude is enhanced. Isoeuphenyl acetate (**D59**) is of quasi-enantiomeric type. "iso- $\gamma$ -Lupene" (**D55**) appears to be anomalous, apparently having the same chirality as the  $\Delta^{13(17)}$ -compounds (**D56-D58**), but a reversed sign of  $\Delta\epsilon$  at  $\lambda_0$ ; the differing side-chain and its possibly differing conformational preference may be responsible.

" $\beta$ "-Equatorial effects. Inspection of 3-isopropylidene-5 $\alpha$ -cholestane (**D1**) shows that the nearest

structural feature contributing asymmetry to the environment of the olefinic group is the " $\beta$ "-equatorial (homoallylic) C(5)-C(6) bond (p. 2504). Bonds geometrically related to the olefinic bond in this manner have been disregarded in the foregoing analysis, but are present in several of the other tetrasubstituted olefins. The bond in question, together with the " $\alpha$ "-equatorial C-C bond, forms a zig-zag closely similar to the "primary zig-zag" of C-C bonds which appears to be responsible for a major part of the CD of carbonyl compounds.<sup>27</sup> Such bonds include those at C(11)-C(12) in  $\Delta^{5(10)}$ -olefins, C(1)-C(2) in  $\Delta^8$ -olefins, C(14)-C(15) in  $\Delta^9$ -olefins, C(10)-C(1) in  $\Delta^{8(14)}$ -olefins, and C(6)-C(7) in the 3,4-dimethyl- $\Delta^3$  olefin (**D8**). In the case of compound **D8**, consignate increments of +0.3 at  $\lambda_0$  and +2.5 at  $\lambda_1$ , taken from data for compound **D1**, improve the agreement between "calculated" and experimental values of  $\Delta\epsilon$ . For the  $\Delta^{5(10)}$ -,  $\Delta^8$ -,  $\Delta^9$ - and  $\Delta^{8(14)}$ -olefins, the suggested increments for " $\beta$ "-equatorial bonds are included in those allotted to " $\alpha$ "-equatorial bonds, but a more refined analysis should perhaps separate these bond contributions.

#### DISCUSSION

*CD at  $\lambda_1$*  (probably the  $\pi_y \rightarrow \pi_y^*$  transition; see below). It is difficult to draw detailed general conclusions from the foregoing analysis. The most obvious feature of the results summarised in Figs. 5, 7, 9-11 is the critical dependence of CD features on the substitution patterns of olefinic bonds. With Yogev *et al.*<sup>7,19</sup> we conclude that the chromophore is not simply the olefinic bond itself, but a composite structure including the olefinic bond with its adjacent allylic (or " $\alpha$ ") bonds. Additional consideration of homo-allylic (or " $\beta$ ") bonds<sup>15</sup> is necessary in some cases to obtain a reasonable correlation of CD with structure.

Although our results show that each class of substituted ethylenes exhibits its own characteristic pattern of behaviour, certain regularities with regard to sign if not magnitude of CD contributions can be discerned throughout the entire series of olefins. The nature of these regularities, outlined below, suggests that the electronic

Structural Type	$\Delta\epsilon$ at $\lambda_1$	$\Delta\epsilon$ at $\lambda_2$
(a) 2-Isopropylidene-decalin	+0.3 (consignate)	+2.5 (consignate)
(b) 1,2-Dimethylcyclohexene: H at ' $\alpha'$ -ax and ' $\alpha'$ -eq	-0.4	+ 8
<u>Increment for:-</u>		
Me at ' $\alpha'$ -ax	-2 (dissignate)	-3 (dissignate)
Me (or CH <sub>2</sub> ) at ' $\alpha'$ -eq	ca.0	+7 (dissignate)
(c) 1-Methyl- $\Delta^{1(9)}$ -octalin H at ' $\alpha'$ -ax	-2	+11
<u>Increment for:-</u>		
Me at ' $\alpha'$ -ax	-2 (dissignate)	-3 (dissignate)

Fig. 11. Tetrasubstituted olefins: CD contributions of structural features.

transition designated as occurring at  $\lambda_1$  is essentially the same transition ( $\pi_y \rightarrow \pi_z^*$ ) for most of the compounds studied; a few highly strained olefins like  $\alpha$ -pinene (C12) may provide exceptions.<sup>21</sup> Some doubt remains, however, concerning the assignments of transitions for tetrasubstituted ethylenes. The CD bands listed under  $\lambda_0$  and  $\lambda_1$  for 3-isopropylidene-5 $\alpha$ -cholestane (D1) both have positive sign; the increments for axial Me substituents (Fig. 11) likewise have the same signs at  $\lambda_0$  and  $\lambda_1$ . Moreover the signs of  $\Delta\epsilon$  at  $\lambda_1$  for "cyclohexenes" (Fig. 7) or "1-methylcyclohexenes" [Fig. 9(i)] match those at  $\lambda_1$  for "1,2-dimethylcyclohexenes" (Fig. 11b).

In each of these cases the sign in question can be correlated with the sense of slight twist which the ring structure might be expected to impose upon the olefinic bond (*cf.* Andersen *et al.*<sup>24</sup>), although olefin torsion for these compounds seems unlikely to reach the value (*ca.* 10°) considered necessary by Levin and Hoffmann in order to outweigh substituent effects.<sup>18</sup> The lack of correspondence between the sign of the CD of twistene and the sign apparently required from the sense of olefin torsion implied by its absolute configuration<sup>28</sup> casts further doubt on explanations which lay emphasis on olefin torsion.

As an alternative hypothesis, the signs of  $\Delta\epsilon$  for "cyclohexenes" can be correlated with the "axial chirality contributions"<sup>7,47</sup> of " $\alpha$ "-quasi-axial C-H bonds. The effects of such bonds would be consignate (compare data for CD at  $\lambda_1$  in Figs. 7 and 11b). Either hypothesis would leave the probability that the generally weak chiroptical effects listed at  $\lambda_0$  for tetrasubstituted olefins belong to a transition which is not normally observed for the other structural types, either because the CD effects are too weak or because they are masked by falling under, or close to, the more pronounced CD curves listed under  $\lambda_1$  for the di- and tri-substituted olefins. Drake and Mason<sup>21</sup> suggested that a Rydberg ( $\pi \rightarrow 3s$ ) band may appear at long-wavelength for certain olefins (e.g.  $\alpha$ -pinene), so this may be the transition in question. The long-wavelength CD bands for some of our tetrasubstituted olefins were *not* significantly shifted in the high-density solvent trifluoroethanol. However, the supposed<sup>21</sup> dependence of the blue-shift of the  $\pi \rightarrow 3s$  band on solvent density is not supported by more recent work.<sup>23</sup> We take the view that  $\lambda_0$  for tetrasubstituted olefins corresponds to a transition not normally observed for the other olefin classes, possibly the Rydberg  $\pi \rightarrow 3s$  band. We therefore label the CD band near 202 nm for tetrasubstituted olefins as  $\lambda_1$ , and compare it with  $\lambda_1$  for the other types of olefins.

The distinction between allylic C atoms in terms of their

relationship to olefinic hydrogen (Figs. 8 and 9) provides a useful basis for discussing alkyl group effects. The data presented with Figs. 5, 7, 9 and 10 show that " $\alpha$ "-alkyl substitution at the allylic carbon *trans* to olefinic hydrogen ( $C_{trans}$  in Figs. 8 and 9) invariably produces a dissignate effect (if any), in comparison with the corresponding compound with " $\alpha$ "-hydrogen; this generalisation is true for either quasi-axial or quasi-equatorial substitution, and applies both to disubstituted ethylenes (of either the *exo*-methylene or the cyclohexene types) and to trisubstituted ethylenes. Tetrasubstituted ethylenes also show dissignate effects of " $\alpha$ "-alkyl groups, although these groups cannot be *trans* to olefinic hydrogen. Our observations for these alkyl substituents correspond to Scott's "reverse octant" rule.<sup>10</sup>

Contrary behaviour is observed for " $\alpha$ "-substitution only in the cases of " $\alpha$ "-quasi-axial Me groups at  $C_{gem}$  (Fig. 9), and possibly for the " $\alpha$ "-quasi-equatorial substitution represented by a "third" ring in  $\Delta^{10}$ -octalin derivatives [bond (*b*) of ring (*z*) in Fig. 10]. The latter example may, however, be due more to " $\beta$ " (homoallylic)-equatorial substitution [bond (*a*) in Fig. 10], since " $\beta$ "-equatorial substitution, where its effect is clearly evident (Figs. 5 and 11a), introduces a considerable consignate contribution; this must account for the observed chiroptical features at  $\lambda_1$  in such compounds as 3-methylene-5 $\alpha$ -cholestane (A13), and at both  $\lambda_0$  and  $\lambda_1$  for 3-isopropylidene-5 $\alpha$ -cholestane (D1). Apparently contrasting behaviour observed<sup>24</sup> for the monocyclic compounds 3-methyl-1-methylenecyclohexane and 3-methyl-1-isopropylidene-cyclohexane has been ascribed<sup>24</sup> to major contributions from non-chair conformations. We have no further information on these compounds.

Homoallylic " $\beta$ "-axial substitution in exocyclic-methylene compounds contributes further major consignate effects, but the dearth of similarly-substituted examples in other classes of olefins leaves uncertainty as to whether the large " $\beta$ "-axial effect is peculiar to the exocyclic-methylene series of compounds.

Comparison of Fig. 5 with similar diagrams representing ring contributions to the CD ( $n \rightarrow \pi^*$ ) of extended *trans*-decalones<sup>27</sup> suggests that zig-zag patterns of C-C bonds may be important for *exo*-methylene compounds and other olefins, although less so than for ketones. Major consignate contributions from " $\beta$ "-equatorial polar groups in compounds of the 3 $\beta$ -substituted- $\Delta^5$  type (Table 6) support the view that bonding patterns may be important. This aspect will be discussed in a future paper.

The widely differing *magnitudes* of the effects of substituents, according to olefin-substitution pattern, may

Table 6. Trisubstituted olefins. Homoallylic substituent effects as typified by 3-substituted- $\Delta^5$  and 7-substituted- $\Delta^4$  steroids

Substituent Group	Conformation	$\delta\Delta\epsilon$ at $\lambda_1^a$	$\delta\Delta\epsilon$ at $\lambda_2^a$
OH	Eq.	2.5 (con.)	9.5 (dis.)
	Ax.	1.5 (dis.)	8 (con.)
OAc	Eq.	1.5 (con.)	3.5 (dis.)
	AX.	4.5 (dis.)	?
Cl	Eq.	5 (con.)	3 (dis.)
	Ax.	2.5 (dis.)	5 (con.)
F	Eq.	3.5 (con.)	?

<sup>a</sup>con. = consignate; dis. = dissignate

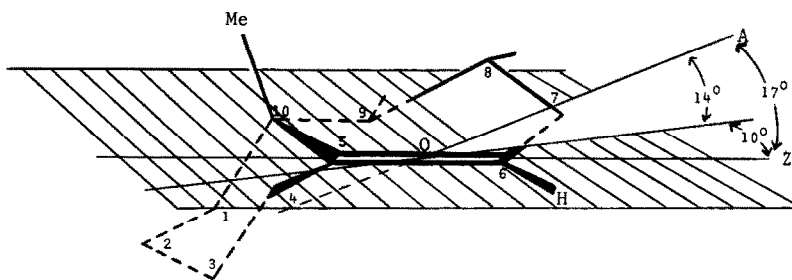


Fig. 12. Cholest-5-ene: Estimated inclination of the axis of polarisation (OA) with respect to the axis (OZ) of the olefinic bond (based upon Fig. 2 in Ref. 19b).

be related to the variable direction of the axis of polarisation of the transition.<sup>19b</sup> An "α"-axial substituent, for example, may lie close to the axis of polarisation in one compound but more distant in another. The diagram (Fig. 12) given for cholest-5-ene,<sup>19b</sup> for example, implies that the 10β-Me group (at  $C_{trans}$ ; Fig. 8) is well away from the axis of polarisation of the transition at  $\lambda_1$ , whereas a 7α-Me substituent (at  $C_{gem}$ ), or a 4β-Me substituent (at  $C_{cis}$ ), is closer to the axis of polarisation. Of these substituents, only that at 10β- gives a large dissignate contribution, the other two having weakly consignate or negligible effects, respectively.

The observation that transitions at  $\lambda_1$  are most sensitive to axial substitution, where bonds to substituent groups have a direction suitable for strong interaction with the p-orbitals which overlap to form the  $\pi_y$  and  $\pi_y^*$  orbitals (Fig. 4), gives support to the view<sup>10</sup> that the transition in question is essentially of  $\pi_y \rightarrow \pi_y^*$  type.

CD at  $\lambda_2$  (probably the  $\pi_y \rightarrow \pi_x^*$  transition). Because of the uncertainties as to the number or assignments of transitions lying at wavelengths below  $\lambda_1$ , any discussion of CD effects listed under  $\lambda_2$  must be only tentative. The main indication of regularity is seen in the reversal of the sign at  $\lambda_2$  compared with that at  $\lambda_1$ , which is observed for most though not all olefins (*cf.* p. 2476). Olefins of the tetrasubstituted class generally conform to the pattern of a sign change between  $\lambda_1$  and  $\lambda_2$ , giving support to the assignments of bonds adopted above and in Table 5. Exceptions occur only in the 5β-methyl-19-nor  $\Delta^9$  (Westphalen) series of compounds, which carry polar substituents in the vicinity of the olefinic bond, possibly introducing additional effects.

Among the other classes of olefins the only notable exceptions to sign reversal occur in the contribution of axial methyl groups at  $C_{gem}$  (Table 9), where CD effects are generally weak, and for compounds which owe a part or all of their CD behaviour to "β"-equatorial alkyl substitution [exocyclic-methylene: Fig. 5; the "third" ring (Z) in Fig. 10]. These are just those systems which are unusual in exhibiting consignate effects of alkyl substitution at  $\lambda_1$ , so the appearance of consignate CD curves also at  $\lambda_2$  puts these compounds in line with the great majority of other olefins with regard to their behaviour at  $\lambda_2$  (i.e. they appear anomalous only at  $\lambda_1$ ).

The most pronounced CD effect noticed at  $\lambda_2$  lies in the very large magnitudes of contributions due to quasi-equatorial alkyl substitution at allylic carbon in compounds of "cyclohexene" type (Figs. 7 and 11). We suggest that strong perturbation by quasi-equatorial substituents provides evidence supporting the  $\pi_y \rightarrow \pi_x^*$  assignment of this transition, since the  $\pi_x^*$  orbital has maximum electron density in the "equatorial" plane of the olefinic bond, where orbital perturbation by interaction

with adjacent quasi-equatorial bonds would be highly favoured.

*Recommendation to users of CD data for olefins.* The analysis of CD data presented in Figs. 5, 7, 9–11 takes account only of the most important structural features contributing to the CD of olefins. Because of the critical dependence of CD curves on detailed patterns of substitution, workers seeking to use the data in this paper as an aid in assigning structures or absolute configurations to new compounds are advised to seek the closest possible analogy among the compounds listed in Tables 2–5. Attempts to calculate values of  $\Delta\epsilon$  for entirely new types of olefins from group increments given in the various Figures are unlikely to produce very reliable results. "Calculated" values of  $\Delta\epsilon$  are expected to be dependable only for relatively simple compounds; the presence of strained rings, 5-membered rings, or polar substituents may introduce deviations which cannot be predicted from present knowledge.

#### EXPERIMENTAL

CD curves were measured for ca. 2–3% solutions in spectroscopic grade n-hexane or methanol, in a 0.5 or 1 mm cell, with a Cary 61 instrument purged with nitrogen.

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*Added in Proof*—Recent work gives support to the view that the longest-wavelength c.d. band ( $\lambda_0$ ) of a tetrasubstituted olefin is due to the  $\pi \rightarrow 3s$  Rydberg transition [A. F. Drake, *J. Chem. Soc. Chem. Comm.* 515 (1976)].

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