A Symmetry Rule for Chiral Olefins

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Summary The Cotton effect sign of the principal $\pi \rightarrow \pi^*$ transition reflects the chirality about the olefin chromophore through an Octant Rule.

THE isolated carbon–carbon double bond exhibits several absorption maxima in the region 180—220 nm. whose assignment (even in the case of ethylene) is still controversial.[1] However, it is generally agreed that the principal absorption band of cycloalkenes,[2] which is shifted to the red by as much as 1 ev on successive alkyl substitution, can be ascribed[3,4] to the $\pi \rightarrow \pi^*$ ($N \rightarrow V$; ${}^1A_g \rightarrow {}^1B_{iu}$) transition ($\epsilon$ 5000—12,000). For chiral olefins, all of the available evidence[1,3–7] suggests that the large rotational strength observed in the region 195—205 nm is in fact derived from the $\pi \rightarrow \pi^*$ transition and that a lower-lying transition of opposite sign[5–7] may well correspond to the $\sigma \rightarrow \pi^*$ absorption which has a predictable non-zero rotational strength. The so-called "mystery band" of olefins whch occurs with only moderate intensity ($\epsilon < 1000$) in solution spectra is most probably the $\pi \rightarrow \sigma^*$ band which has almost zero magnetic moment and thus a vanishingly small rotational strength. For the majority of olefins we can thus assume that the lower energy Cotton effect is associated with a $\pi \rightarrow \pi^*$ absorption and that the $\pi \rightarrow \sigma^*$ band which appears as a shoulder on the red side of the $N \rightarrow V$ excitation will be devoid of optical activity.[4] With the clarification of these assignments we can now show that the absolute configuration of a chiral olefin can be derived from the appropriate symmetry considerations, which, as adumbrated by Schellman,[8] lead to an octant rule.

Using the intersecting *xy*, *xz*, and *yz* symmetry planes of ethylene (point group D_{2h}) as octant interfaces (Figure 1) the olefin is viewed in the *z* (or $-z$) direction. The octant signs are derived empirically from the octant location of substituents of several steroidal olefins of known absolute configuration using Dreiding models and octant diagrams analogous to those developed for the carbonyl rule.[2,10] The observed and predicted Cotton effect signs (near 200 nm.) of some representative olefins are shown in the Table.

By way of illustration we may consider some Δ^5-steroidal olefins (Figure 2). Thus, whilst 19-norcholest-5-ene (R =H,

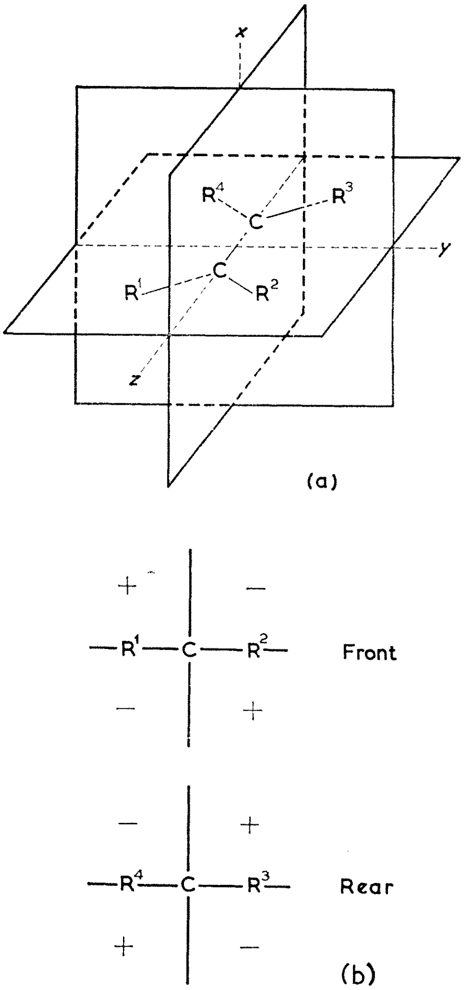
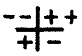


FIGURE 1. *Octant diagram for chiral olefins showing* (a) *intersecting symmetry planes* xy, yz, xz, *and* (b) *the corresponding front and rear octants viewed along the* z *axis.*

TABLE

Predicted and observed‡ Cotton effects (C.E.) of olefins

Olefin	Front octants	Rear octants	C.E. Predicted sign	C.E.† Observed sign (195—205 nm)
Cholest-1-ene†			−	−
Cholest-2-ene‡			+	+
Cholest-3-ene†			−	−
Cholest-4-ene‡			−	−
17β-Hydroxyoestr-4-ene[6]			+	+
17β-Hydroxyoestr-5-ene[6]			−	−
Cholest-5-ene‡			+	+
4,4-Dimethylcholest-5-ene[7]			−	−
Androst-9(11)-ene[6 7]			+	+
‡(−)-β-Pinene*			+	+
‡(+)-α-Pinene*			+	+
R-trans-(−)-cyclo-octene‡			−	−

* The rotativity contribution of the cyclobutyl grouping may dominate the optical activity in these cases (see refs. 9 and 10).
† *Cf.* refs. 6, 7.
‡ Measured as a c.d. maximum near 200 nm. Only the signs are reported in the Table. Accurate Δε values and rotational strengths will be published in the full paper. We thank Dr. G. D. Meakins (Oxford) for a gift of some steroidal olefins.

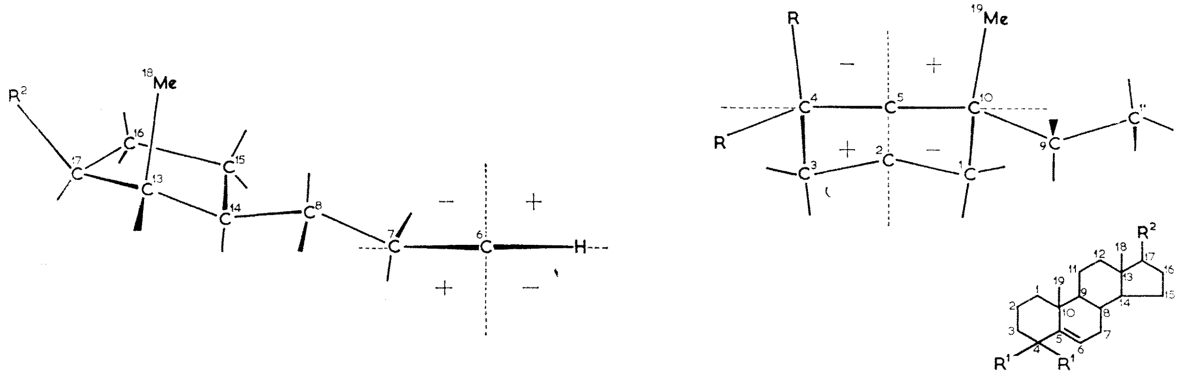


FIGURE 2. *Octant diagram for Δ⁵-olefins showing* (a) *rear octants viewed from* C-5 *to* C-6 (b) *rear octants viewed from* C-6 *to* C-5

19-methyl replaced by H) has a negative Cotton effect, cholest-5-ene (R = H) is positive and the addition of a further methyl group in a negative octant in lanost-5-ene (R = Me) again reverse the sign to give a negative c.d. The inclusion of the optically active *trans*-cycloalkenes indicates a merging of the models for inherently dissymmetric chromophores and the asymmetric perturbation of symmetric transitions. Thus, from symmetry considerations alone, the absolute configuration (*R*) may be assigned[11] to both (–)-*trans*-cyclo-octene and (–)-*trans*-cyclononene (Figure 3), suggesting that the twisted olefin model is less important[1d,12] in these systems than the occupation of appropriate octants by methylene groups. The formulation of any chirality rule requires predictive as well as correlative success. In this regard it will be of interest to measure the $\pi \rightarrow \pi^*$ Cotton effect signs of several classes of olefins whose substituents reflect the same (or similar) degree of atomic refractivity or rotativity order in influencing the Cotton effect sign as that found for the carbonyl $n \rightarrow \pi^*$ transition.[10] This would imply a reversed octant rule[13] for substituents such as cyclopropane, epoxide, fluorine, and methoxy which on the refractivity scale fall well below alkyl, Br, Cl, and I substituents. Similarly it will be of interest to test the underlying basis of Mills' rule[14] for allylic alcohols in terms of the effect of placing hydroxy-groups in various octants in the immediate vicinity of the double bond. A useful regional chirality rule[7] requiring the presence of allylic quasi-axial carbon–hydrogen bonds can be accommodated within the octant rule.

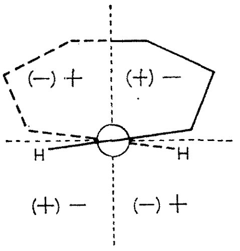


FIGURE 3. *Octant diagram for* (R)-(–) trans *cyclo-octene* (*Newman projection*). *Rear octant substituents are shown thus* (- - - - - - -). *Rear octant signs are in parentheses.*

Further application of the olefin octant rule to compounds containing additional chromophores may be limited, since the presence of other optically-active transitions in the region 185—210 nm. will interfere. In these cases it may be necessary to use other methods of assignment.[15]

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