On the Chirality of the Isolated Double-bond Chromophore

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THE u.v. spectra of mono-olefins show a high-intensity band at $\lambda_{max} < 200$ mμ (defined as a $\pi \rightarrow \pi^*$ transition). In addition, another band of lower intensity is observed in the vapour phase at $\lambda > 200$ mμ which has recently been assigned to a $\pi \rightarrow \sigma^*$ transition.[1] In solutions, this longer-wavelength band is shown mainly by highly substituted ethylenes.[2] We report that the o.r.d. spectra of mono-olefins in solution exhibit a Cotton effect which may be related to the latter u.v. band, as well as a background rotatory dispersion related to other transitions, possibly including the $\pi \rightarrow \pi^*$ one.

The o.r.d. measurements[†] of a number of steroidal mono-olefins were extended to a shorter-wavelength region than had been previously recorded[3] (in some compounds down to *ca.* 190 mμ). In several cases, including the 19-nor-Δ^4- and 19-nor-Δ^5-steroids, the Cotton effect is relatively well resolved from the background rotatory dispersion (Figure 1). In other compounds, as in Δ^4- and Δ^5-steroids, the Cotton effect is superimposed on a much stronger background curve (Figure 2). It is apparent from the shape of the resulting curves that the sign of the Cotton effect is generally opposed to that of the background. The sign of the optical rotation at high wavelength, $\lambda > 230$ mμ[4] (in most cases up to the

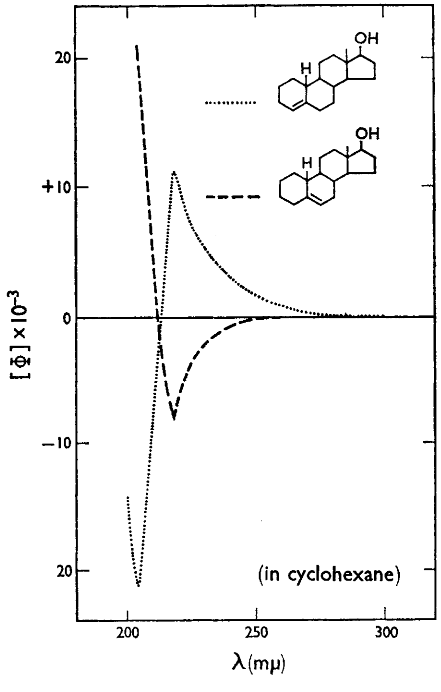

FIGURE 1.

[†] The o.r.d. measurements were performed on a JASCO model ORD/UV-5 instrument in cells of 1, 0·1, and 0·01 mm. width.

sodium D-line) is determined rather fortuitously by either the Cotton effect or the background rotation, and therefore cannot in itself serve to predict the sign of either.

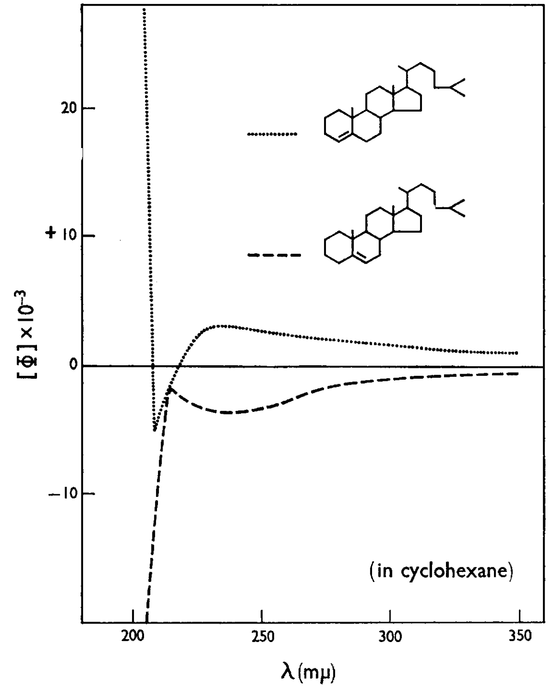

FIGURE 2.

The o.r.d. Cotton effects observed by us reflect the c.d. maxima reported by Legrand and Viennet.[5] The signs of the observed Cotton effects (Table) correspond to the signs of the c.d. maxima of similar types of compounds. The shape of some of the c.d. curves at the shorter-wavelength branch suggest an additional effect which may correspond to our background curve.‡

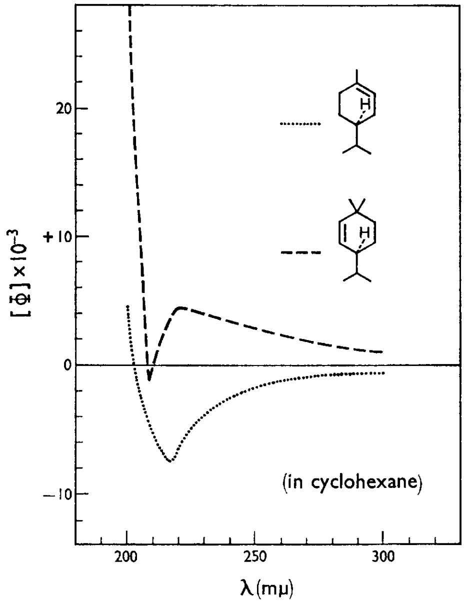

FIGURE 3.

The relation between the position of the double bond in the steroidal molecule and the sign of the Cotton effect indicates that the latter may be dependent on the asymmetric environment of the double bond.[4] We define a dissymmetric chromophore responsible for this Cotton effect as containing the double-bond carbon atoms and their allylic quasi-axial hydrogens. This rotophore

TABLE

Compound	Axial H atom	Sign of the Cotton effect	Sign of rotation at λ_{230}
Cholest-1-ene	3α(−)	−	+
Cholest-2-ene	1α(+), 4β(+)	+	+
Cholest-3-ene	2β(−), 5α(−)	−	+
17β-Acetoxy-5β-androst-3-ene	2α(+), 5β(+)	+	−
Cholest-4-ene	3α(+), 6β(−)	−	+
17β-Hydroxyœstr-4-ene	3α(+), 6β(−), 10β(+)	+	+
Cholest-5-ene	4β(+), 7α(−)	+	−
4,4′-Dimethylcholest-5-ene	7α(−)	−	−
17β-Hydroxyœstr-5-ene	4β(+), 7α(−), 10β(−)	−	−
3β,17β-Diacetoxyandrost-7-ene	6β(−), 9α(−), 14α(+)	−	−
Androst-9(11)-ene	8β(+), 12α(+)	+	+
5β-Androst-9(11)-ene	8β(+), 12α(+)	+	+

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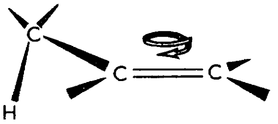
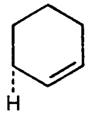
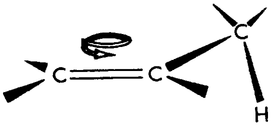
‡ A quantitative comparison of the c.d. and o.r.d. data is not possible since an accurate value of the Cotton effects cannot be obtained, due to their superposition on a background curve. Moreover, the respective c.d. curves (ref. 5) may also be composite.

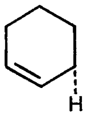
will have a positive Cotton effect when arranged in a positive helix represented geometrically as follows:





and a negative Cotton effect when in a negative helix:





When more than one quasi-axial hydrogen atom is present in the allylic positions to the double bond, the Cotton effect of the system may depend on the sum of the contributions of all the quasi-axial hydrogens. As an insufficient number of types of olefins had been measured, we did not attempt to establish the relative contribution of ***each*** axial hydrogen atom to the sign of the Cotton effect. Furthermore, there may be factors in the rest of the asymmetric environment which influence the sign of the Cotton effect to a lesser degree. From the examples given in the Table it appears that an axial allylic methyl group plays a smaller role in determining the sign of the Cotton effect. This sign is in accord with our definition in all the examples given, excepting the Δ^4- and Δ^5-normal steroids, where it cannot be predicted, since the two quasi-axial hydrogens in both compounds have an opposite helicity in relation to the double bond. The negative Cotton effect observed in both (+)-*p*-menth-2-ene and (−)-*p*-menth-2-ene (Figure 3) is also in agreement with the chirality of their double bond rotophore.

It appears that the u.v. spectra of mono-olefins in solution are generally due to a superposition of at least two bands. The one at $\lambda > 200$ mμ is not observed in many olefins because its low absorption intensity is covered by the much stronger, shorter-wavelength transitions. This correlation of the longer-wavelength transition with the observed Cotton effect is supported by the following observations: (1) In some olefins when methanol was replaced by cyclohexane as solvent an increase was observed in both the apparent $[\Phi]_{\max}$-value of the first extremum of the Cotton effect, and the absorption intensity at $\lambda > 200$ mμ. (2) In a series of olefins with the same degree of substitution an increase of the apparent $[\Phi]_{\max}$-values of the Cotton effect was found to be accompanied by an increase in the u.v. absorption intensity at $\lambda > 200$ mμ.

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