Linear and Circular Dichroic Study of Mono-olefins

By Ammnon Yogev,* Jacob Sagiv, and Yehuda Mazur*

(*Department of Chemistry, The Weizmann Institute of Science, Rehovot, Israel*)

Summary An analysis of the circular and linear dichroic spectra of exocyclic olefins substantiates the view that the octant rule cannot be applied to the higher wavelength Cotton effects of olefins.

Mono-olefins generally show a broad and diffuse u.v. spectrum with a maximum at *ca.* 180—210 nm.[1] On the other hand the c.d. spectra of chiral olefins, present two distinct Cotton effects, one having its maximum at *ca.* λ 200 nm and the other at *ca.* λ 190 nm.[2-4]

Recent measurements of linear dichroic (plane polarized) u.v. absorption spectra of Δ^4- and Δ^5-cholestenes, oriented in stretched films, showed that the broad u.v. band is composed of two transitions: λ_1, at *ca.* 185 nm (ϵ 8 $\times$ 10^3) polarized along the double bond and λ_2, at 202—205 nm (ϵ 4 $\times$ 10^3) whose polarization deviates from the double bond axis by *ca.* 16·5°.[5] Comparison of the maxima of the resolved u.v. spectra of Δ^4- and Δ^5-cholestenes with those of the respective c.d. curves ($\lambda < 185$ and 200 nm) reveals that the two Cotton effects are associated with the same λ_1 and λ_2 transitions (Figure 1).

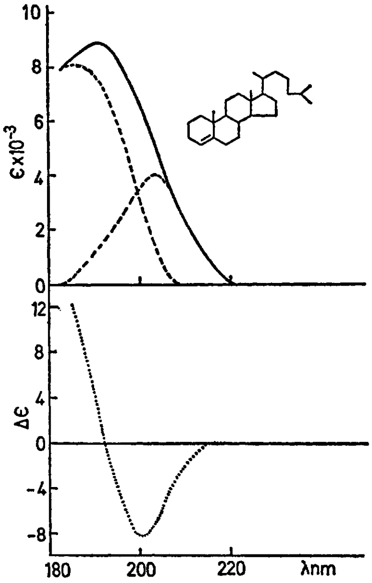

Figure 1. Δ^4-*Cholestene;* (———) *isotropic and* (– – –) *resolved u.v. absorption spectrum;* (············) *c.d. spectrum.*

In most endocyclic olefins the c.d. maxima of the two transitions are well separated and the assignment of their signs appears unambiguous.[2-4] However, in exocyclic olefins the two maxima are sometimes very close, making the assignment of signs difficult.[6,7] This may be exemplified by the c.d. curve of 3-methylene-5α-cholestane (Figure 2), which exhibits two positive maxima of which the one at longer wavelength, λ_2, was assigned a negative sign.[7]

In order to establish unequivocally the signs of the Cotton effects in this compound we have measured its polarization spectrum, namely, we have incorporated this compound into a stretched film and measured its u.v. spectrum using light polarized in the direction of stretching ($\epsilon_{\parallel}$) and orthogonal to it ($\epsilon_{\perp}$). The resulting dichroic ratios, $d_0 = \epsilon_{\parallel}/\epsilon_{\perp}$, showed wavelength independent values only at the extreme short and long wavelength portions of the spectrum indicating the superposition of two partly overlapping bands. Using these constant d_0 values we have resolved the isotropic u.v. spectrum (λ_{max} 194 nm, ϵ 10,600) into two bands (λ_{max} 188 and 200 nm, ϵ 8700 and 6500) as shown in Figure 2. The maxima of the resolved spectrum of 3-methylene-5α-cholestane are further apart than those of the apparent c.d. maxima (λ_{max} 188 and 195 nm) indicating that the latter represents a superposition of two positive Cotton effects.

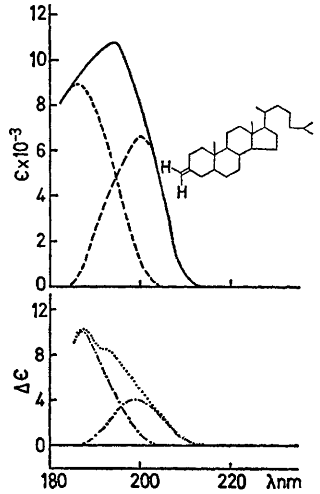

Figure 2. 3-*Methylenecholestane;* (———) *isotropic and* (– – –) *resolved u.v. absorption spectrum;* (············) *experimental and* (–·–·–) *resolved c.d. spectrum.*

We have drawn the hypothetical c.d. curves for the two transitions, based on the assumption that the long and the short wave-length segments of the experimental curve represent the c.d. of a pure transition with a constant dissymmetry ratio $\Delta\epsilon/\epsilon$ (Figure 2). The sum of the two resolved c.d. curves approximates to the experimental c.d. spectrum.

Using the same method, we have also separated the isotropic u.v. spectrum of 3-isopropylidene-5α-cholestane

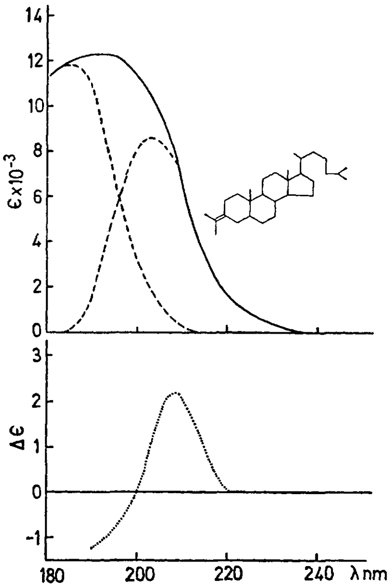

FIGURE 3. *3-Isopropylidenecholestane:* (———) *isotropic and* (– – –) *resolved u.v. absorption spectrum;* (············) *c.d. spectrum.*

(Figure 3). Since the maxima of the two u.v. bands (λ 190 and 204 nm) are closer than those of the c.d. ($\lambda < 190$ and 208 nm), the two Cotton effects have respective negative and positive signs (Figure 3). Separation of the c.d. curve resulted in a curve similar in shape to the experimental one. These results are at variance with the generalization that the two Cotton effects are always of opposite sign[7] and also with the octant rule recently suggested[4,8] for the λ_2 bands of olefins which predicts a negative sign for this band in the latter two olefins.

The failure of the olefin octant rule is not surprising in view of our finding that the transition moment of the λ_2 band does not necessarily coincide with the direction of the double bond which serves in this rule as the octant interface.[5] On the other hand these results substantiate our previous suggestion that in the correlation of the Cotton effect of an olefin with its absolute configuration, both the double bond and its neighbouring σ-bonds should be regarded as a dissymmetric chromophore.[3]

(*Received, 26th January* 1972; *Com.* 116.)

---

[1] A. J. Merer and R. S. Mulliken, *Chem. Rev.*, 1969, **63**, 639; D. W. Turner, *J. Chem. Soc.*, 1959, 30; R. A. Micheli and T. H. Applewhite, *J. Org. Chem.*, 1962, **27**, 345.

[2] M. Legrand and R. Viennet, *Compt. rend.*, 1966, *C*, **262**, 1290; A. Yogev and Y. Mazur, *Chem. Comm.*, 1965, 552.

[3] A. Yogev, D. Amar, and Y. Mazur, *Chem. Comm.*, 1967, 339.

[4] A. I. Scott and A. D. Wrixon, *Tetrahedron*, 1970, **26**, 3695; 1971, **27**, 4787.

[5] A. Yogev, J. Sagiv, and Y. Mazur, submitted for publication to *J. Amer. Chem. Soc.*

[6] M. Fetizon and I. Hanna, *Chem. Comm.*, 1970, 462.

[7] M. Fetizon, I. Hanna, A. I. Scott, A. D. Wrixon, and T. K. Devon, *Chem. Comm.*, 1971, 545.

[8] P. Crabbé, "An Introduction to the Chiroptical Methods in Chemistry", Mexico 1971, 19—22; P. M. Scopes, *Ann. Reports*, 1968, 66B, 36.