

Cotton Effect of Isolated Double Bonds in Steroidal Olefins

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It has been postulated that a distortion of a double bond from planarity may lead to a pronounced Cotton effect of the $\pi \rightarrow \pi^*$ transition. The magnetic moment necessary to generate the rotatory power of this transition would then be provided by the contribution of the transition moment perpendicular to the direction of the electric dipole moment.¹ On the other hand it may be argued that the $\pi \rightarrow \pi^*$ transition of a planar double bond can also generate a high rotational strength, provided the double bond is embodied in a dissymmetric milieu. The needed

magnetic moment might be donated by the σ -orbitals perturbing the $\pi \rightarrow \pi^*$ transition.

We measured the o.r.d. curves of a few steroidal olefins on a JASCO Model ORD/UV-5 instrument, in cyclohexane solution, using cells of 0.1 cm. path length. The results recorded in Figures I and II indicate that some of the olefins show a pronounced first extremum of a Cotton effect. Furthermore, it may be observed that the sign of the rotational values at the higher wavelengths does not represent necessarily the sign of the Cotton effect. It was previously reported²

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¹ A. Moscowitz and K. Mislow, *J. Amer. Chem. Soc.*, 1962, **84**, 4605.

² P. Crabbé, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Holden-Day, San Francisco, 1965, pp. 32-33, 67-70.

that the sign of the o.r.d. curves up to *ca.* 300 $m\mu$ in some steroidal and terpenoidal olefins indicates a symmetry relationship in respect to the allylic

first extremum of the Cotton effect. It seems therefore that the rotatory strength of the double-bond transition in the compounds studied depends

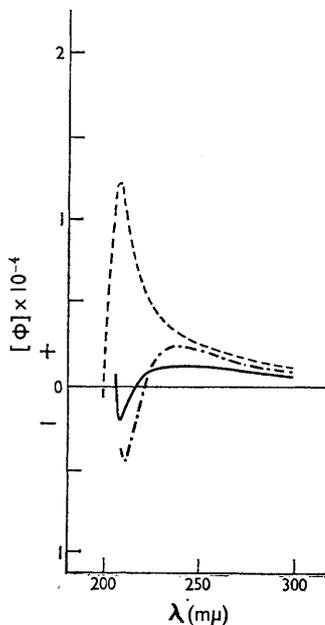


FIGURE I

— 5 α -Cholest-1-ene. - - - 5 α -Cholest-2-ene.
 - · - · Cholest-4-ene

ring junction (*e.g.* to the C-10 position in cholest-5-ene and cholest-4-ene). We wish to emphasize that the sign of the Cotton effect does not reflect this symmetry relationship. In addition no significant distortion of the double bond can be visualised in the steroidal olefins showing a high

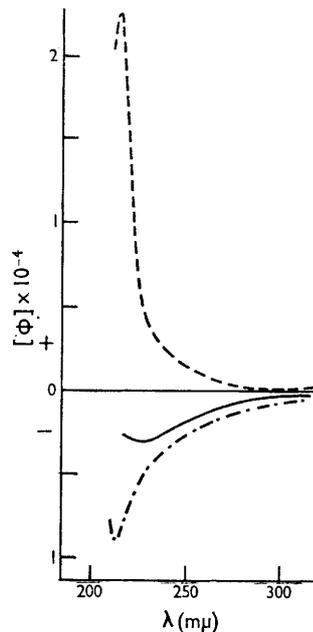


FIGURE II

- - - 5 α -Androst-9(11)-ene. — Cholest-5-ene.
 - · - · 4,4-Dimethylcholest-5-ene

strongly on their dissymmetric environment. A qualitative relation between the two may eventually emerge, provided a large amount of data on olefins is compiled.

(Received, October 8th, 1965; Com. 636.)