The Circular Dichroism of Methylene-steroids

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Summary The Cotton effect of various methylene-steroids, mainly in the androstane series, is discussed; its sign does not fit the recent rule of Scott and Wrixon.

ALTHOUGH many data are available on the circular dichroism associated with the $n \rightarrow \pi^*$ transition of ketones, especially in the steroid series,[1,2] the Cotton effect of the formally related methylene-steroids has not been determined. Until very recently,[3,4] only a few mono-unsaturated substances have been studied in this respect.

The main difficulty one has to face, in order to interpret the sign of Cotton effects in terms of structural features, is due to the high complexity of the absorption band of olefins in the 200 nm region, which has long been considered an intractable problem.[5] Yaris, Moscowitz, and Berry[6] have shown that at least three transitions must be taken into account.

(a) The $\pi_z \rightarrow \pi_z^*$ (usually $\pi \rightarrow \pi^*$ or $V \leftarrow N$) transition, which is the major phenomenon as long as only *oscillator, but not rotational, strength* is considered.

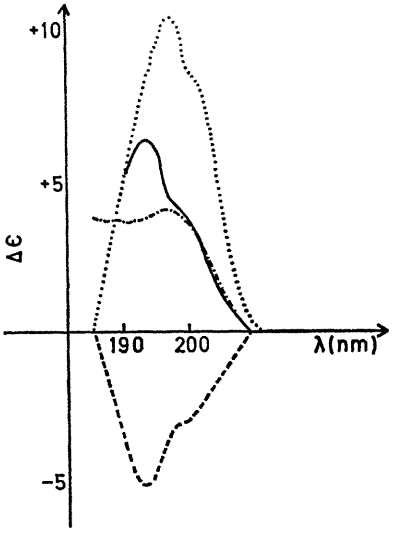
(b) The Rydberg-like transition $\pi_z \rightarrow 3s\sigma$ of Price[7] and Mulliken,[8] which is also allowed. However, the associated rotational strength is very low.

(c) Another Rydberg-like transition, pictured as a $\pi_z \rightarrow 3p\pi y$ transition, which is electric-dipole-forbidden, but electric-quadrupole- and magnetic-dipole-allowed. Although its contribution to absorption is comparatively low, it may outweigh the $\pi_z \rightarrow \pi_z^*$ contribution to Cotton effect, at least in twisted olefins.

In other words, the observed Cotton effect is due to at least two contributions, *which may have opposite signs.*

This, *a priori*, rules out any attempt to interpret the sign of the resulting effect in terms of a simple octant rule, on a very broad basis.

In fact, almost none of the examples of non-twisted olefins, which we have studied, fit the recent rule of Scott and Wrixon,[4] *the scope of which may be limited to twisted olefinic compounds.*



FIGURE

—— 3-*Methylene-5α-androstane*; - - - 3-*Methylene-5β-androstane*; · · · · 2-*Methylene-5α-androstane*; ·-·-·6-*Methylene-5α-androstane.*

The experimental data are shown in the Table.†

† The curves were recorded on a Roussel Jouan Dichrograph Model 2, in hexane, at room temperature, by Mrs Picot, Institut de Chimie des Substances Naturelles, Gif-sur-Yvette, whose help is acknowledged.

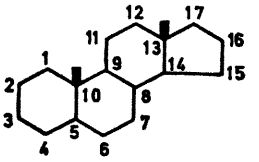
The following remarks may be made:

(a) The intensity of the Cotton effect of methylene steroids is larger than the intensity of the Cotton effect exhibited by the related ketones.

(b) With the exception of 6-methylene-5α-androstane, these two effects have the same sign.

(c) The Cotton effects of two remote methylene group are additive (in terms of integrated intensity).

C.d. of methylene-steroids (in hexane)



	Compound	λ_{max}	$\Delta\epsilon_{max}$
(1)	1-Methylene-5α-androstane	199	−2·2
(2)	2-Methylene-5α-androstane	197	+10·5
(3)	3-Methylene-5α-androstane	193	+6·4
(4)	3-Methylene-5β-androstane	199 193	−3 −5·1
(5)	4-Methylene-5α-cholestane	200	−10·5
(6)	6-Methylene-5α-androstane	197	+4·2
(7)	6-Methylene-3α,5-cycloandrostane	203	+12·8
(8)	7-Methylene-5α-androstane	No maximum	<0
(9)	16-Methylene-5α-androstane	193	−7·9
(10)	17-Methylene-5α-androstane	193	+3·8
(11)	20-Methylene-5α-pregnane	190 201	−2·4 +1·8
(12)	17-Methylene-18-nor-D-homo-5α-androstane	192	−5·16
(13)	2-Methylene-A-nor-5α-androstane	202	+3·8
(14)	3,17-Dimethylene-5α-androstane	193	+18·4
(15)	3,17-Dimethylene-5β-androstane	188 200	−2·5 +5
(16)	3,6-Dimethylene-5α-androstane	188 197 205	−11 +6·1 −2·8
(17)	6,17-Dimethylene-5α-androstane	195	+5·5
(18)	3,20-Dimethylene-5α-pregnane	199	+6

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