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HOMOALLYLIC AXIAL CHIRALITY BOND CONTRIBUTIONS TO THE $\pi\rightarrow\pi^*$ COTTON EFFECTS OF OLEFINS

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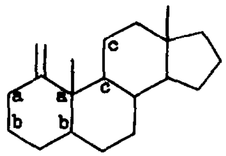
Both the allylic axial chirality[1] and the left-handed olefin octant[2] rules in most cases correctly predict the sign of the long wavelength $\pi\rightarrow\pi^*$ transition Cotton effect. However in certain cases, e.g. in exomethylene steroids[2,3], apparent limitations were found. Searching for the method of quantitative olefin c.d. correlations we have come to the conclusion that homoallylic axial substituents play eqally important role as the allylic axial substituents do. This conclusion rests on the simple model of the inherently symmetric chromophore dissymmetrically perturbed in the excited state by nonbonded interactions /dipole-dipole type/ with the substituents in its proximity. The rotational strength contribution of the substituent depends on its nature and its vectorial distance from the chromophore, the sign being determined by allylic axial chirality[1] or the right-handed octant rule. In exomethylene steroids having ketone-like ring geometry the distances between the chromophore and either allylic axial /a/ or homoallylic axial /b/ substituents are similiar, hence the contribution of the homoallylic substituent is expected to be of the same magnitude, or even greater than that of the allylic substituent. Moreover, other interactions of homoallylic character /c/ have to be taken into account, which exhibit much smaller /sometime negligible/ contributions to the magnitude of the Cotton effect[4].



Example - axial chirality bond contributions to the $\pi\rightarrow\pi^*$ Cotton effect of 1-methylene-5α-androstane:
a = 2βH,10βMe; b = 3αH,5αH; c = 9αH,11βH

In any position the axial methyl substituent shows ca. 1.5 times stronger contribution than the axial methine /tertiary/ C-H bond and this in turn gives 1.5-2 times stronger contribution than the axial methylene /secondary/ one.

The examples collected in the Table are illustrative for this approach.

Our approach can be successfully applied to many other endocyclic olefins[2,5,6], taking into account that different ring geometry may change the rotational strength contributions of the substituents. The only exceptions observed are cholest-4-ene and cholest-5-ene, but not their 19-nor analogs. The possible application of this approach to optically active dienes constitutes an extension of the existing rules[7]. Homoallylic axial chirality bond contributions are also expected to be a key for quantitative treatment of the Cotton effects in olefinic systems.

Table

Comparison of observed and predicted magnitudes of the Cotton effects of exomethylene steroids[a]

Compound and c.d. maximum		Chirality contributions		
observed		negative		positive
1-Methylene-5α-androstane	-2.2 /199 nm/	2βH,5αH,9αH,11βH[4]	>	3αH,10βMe
2-Methylene-5α-androstane	+10.5 /197 nm/	1αH,4βH	≪	3αH,10βMe
3-Methylene-5α-androstane	+6.4 /193 nm/	1αH,4βH	<	2βH,5αH
3-Methylene-5β-androstane	-3 /199 nm/	2αH,5βH	>	1βH,4αH
4-Methylene-5α-androstane	-10.5 /200 nm/	3αH,6βH,10βMe	≫	2βH,5αH
6-Methylene-5α-androstane	+4.2 /197 nm/	5αH,8βH	<	4βH,7αH,10βMe
7-Methylene-5α-androstane	ca. 0	5αH,8βH	≈	6βH,9αH,14αH
3β-Acetoxy-11-methylene-5α,25D-spirostan[b]	-3.2 /200 nm/	1αH,8βH,10βMe,12αH[4]	>	9αH,13βMe
17-Methylene-18-nor-D-homo-5α-androstane	-5.0 /192 nm/	13βH,16αH	>	15βH,17aαH
2-Methylene-A-nor-5α-androstane	+3.8 /202 nm/	pseudoaxial 1αH,3βH[8]	≪	5αH,10βMe
16-Methylene-5α-androstane	-7.9 /193 nm/	13βMe,14αH	≫	ps.ax. 15βH,17αH[8]
17-Methylene-5α-androstane	+3.8 /193 nm/	13βMe[8]	<	12αH,14αH,15βH

[a] Data from ref. 3, except where noted.   [b] Data from ref. 2.

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