Diene Geometry and Allylic Axial Chirality Effect

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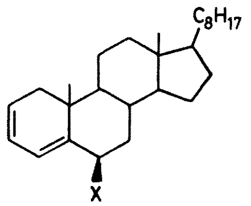
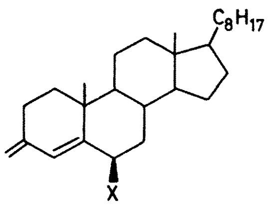
Summary The sense of the contribution of polarizable allylic axial bonds to the π–π* Cotton effect of dienes is found to be determined by the chirality of the system which is defined by the direction of the transition moment and direction of the allylic bond

The concept of allylic axial bond contribution to the lowest energy π–π* Cotton effect of simple olefins[1] and conjugated systems[2] is now well established and accepted Its importance was demonstrated particularly well for polarizable allylic bonds[3] and for allylic bonds in homoannular positions of skewed cyclohexa-1,3-dienes [4]

We have now found that the sense of the allylic axial chirality contribution depends on the direction of the lowest energy π–π* transition moment in conjugated dienes In order to identify clearly the allylic axial bond effect we have examined chiroptical properties of the steroidal *s-cis-* and *s-trans-*dienes (**1**) and (**2**) having allylic C–X bonds with good donor–acceptor abilities (Table)



(1)



(2)

The P-helicity *s-cis*-diene (**1a**) exhibits, as expected, a positive lowest energy π–π* Cotton effect By introducing polar substituents in the allylic axial 6β-position the Cotton effect is significantly enhanced, thus demonstrating the *positive* chirality contribution of the C–X bond in (**1b**–**1d**), in apparent disagreement with traditional understanding of the allylic axial chirality rule On the other hand, the C–X bond in the same allylic axial 6β-position in the

TABLE. Chiroptical data of the dienes (**1**) and (**2**).[a]

	X	Lowest π–π^* transition c.d.	(λ/nm)	u.v.	(λ/nm)	Higher energy c.d. bands	Solvent
(**1a**)	H	+12·6	(265)	6425	(265·5)	+2·75 (214·5)	Heptane[b]
(**1b**)	OH[c]	+17·5	(264)	6370	(264)	+5·5 (222)	Heptane
(**1c**)	NHEt	+20·8	(265)	6400	(266)	+1·2 (217)	Dioxan
(**1d**)	NHAc	+26·3	(264)	6760	(267)	+1·8 (220)	Dioxan
(**2a**)	H	+15·0	(237)	25,420	(239)	−5·1 (196)	Heptane[b]
(**2b**)	OH	+7·85	(239)	26,000	(239·5)	−13·65(196)	Heptane
(**2c**)	OAc	+2·4 +3·4	(249) (238)	25,900	(241)	+8·3 (223)[d] −6·3 (197)	Heptane
(**2d**)	NHAc	+0·8 −0·8	(253) (243)	23,600	(242)	+14·4 (221)[d]	Dioxan

[a] C.d. measurements with a Jobin–Yvon III Dichrograph. The *cis*-dienes (**1**) were prepared from the corresponding tosylhydrazones by reaction with Bu^{n}Li, except for (**1c**) which was prepared from (**1d**) by $LiAlH_4$ reduction. The *trans*-dienes (**2**) were prepared from the corresponding ketones by Wittig reactions except for (**2c**) which was prepared from (**2b**) by acetylation.
[b] Data in dioxan are practically identical. [c] Physicochemical data were in agreement with those reported (J. M. Coxon, M. P. Hartshorn, and C. N. Muir, *Tetrahedron*, 1969, **25**, 3925). [d] Cotton effect is most probably due to local excitation in –X.

s-trans-dienes (**2b–d**) gives a *negative* contribution to the π–π^* Cotton effect; while the essentially planar diene (**2a**) exhibits a strong positive Cotton effect, its 6β-substituted derivatives (**2b–d**) show diminished Cotton effects. Thus the effect of 6β-substituent in the dienes (**2**) [see (B) in the Figure] is of the same sense as the effect of a 6β-hydroxy-substituent on the lowest energy π–π^* transition Cotton effect in steroidal Δ^4-olefins[5] [(A) in the Figure], but it is of opposite sense in the dienes (**1**) [(C) in the Figure].

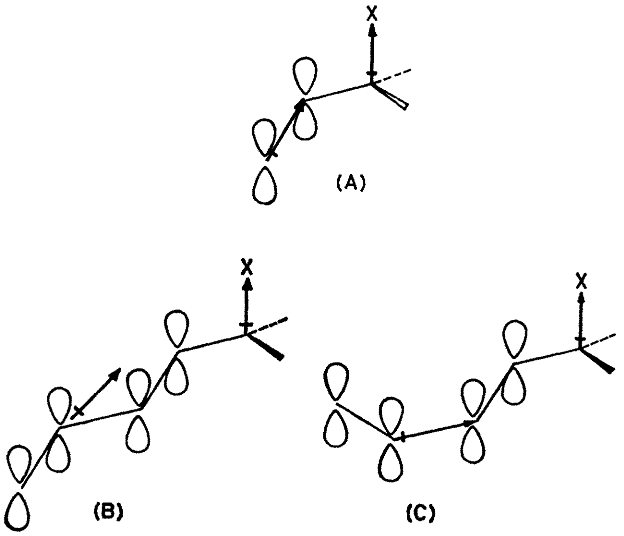


FIGURE. Chirality contributions of allylic axial C–X bonds: (A) olefin (−ve); (B) *trans*-diene (−ve); (C) *cis*-diene (+ve).

It should be emphasized that conformational changes in rings A and B due to 6β substitution in (**1b–d**) and (**2b–d**) are insignificant, as shown by the shape of the 6α-H n.m.r. signal in these compounds; hence they cannot account for substantial changes in chiroptical properties of the dienes (**1**) and (**2**).

The failure of the traditional understanding of allylic axial chirality contributions to account for Cotton effects of (**1b–d**) can be easily surmounted if transition moments are considered. These are given in the Figure, as determined by recent linear dichroism studies.[6] On the basis of our experimental findings we propose that the contribution of allylic axial bonds in conjugated systems is determined by its chiral relation to the chromophore transition moment [(B) and (C) in the Figure] rather than by chiral perturbation of the nearest double bond component.

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