

OPTICAL ROTATORY DISPERSION AND CIRCULAR DICHROISM PART LXXVIII.¹

THE CIRCULAR DICHROISM OF THE STEROID HYDROCARBON SKELETON

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(Received in UK 27 February 1973; accepted for publication 8 March 1973)

In connection with our recent work on the short wavelength c.d. of alcohols,² ketones³ and other chromophores,⁴ we noted significant differences in the dichroism below 190 nm between pairs of compounds, identical in all respects apart from the configuration at C-5 in the steroid skeleton (5 α -H or 5 β -H). This prompted us to examine the c.d. of some totally-unsubstituted hydrocarbons below 200 nm, and the results (listed in the Table) establish that c.d. can be observed for chiral steroid hydrocarbons in this region of the spectrum. Mason⁵ has previously observed c.d. in the strained cage-like saturated hydrocarbon (+)-twistane ($\Delta\epsilon$ +0.7 at 187 nm in iso-octane), but this compound cannot be regarded as typical of alicyclic hydrocarbons.

The essential series of four androstanes differing in configuration at C-5 and C-14 was described recently⁶ and we are greatly indebted to Prof. N.L. Allinger (University of Georgia) for generously providing samples for this work. Pairwise comparisons of data for the isomeric androstanes show that $\Delta\epsilon$ at the shortest wavelength reached (183-184 nm) is more positive for the 5 β than for the 5 α compounds (differences: $\Delta\epsilon_{5\beta} - \Delta\epsilon_{5\alpha}$, +1.3, +1.9, +0.6 units) and more negative for the 14 β than for the 14 α isomers (differences: $\Delta\epsilon_{14\beta} - \Delta\epsilon_{14\alpha}$, -1.7, -1.1 units). The numerically larger values of $\Delta\epsilon$ occur for the isomers with one cis junction; we therefore suggest that the observed dichroism is associated mainly with the inherent chirality of a rigid cis-fused bicyclic system. Models show that the chiral A/B ring system in a 5 β -steroid is of roughly enantiomeric type to the C/D ring system in a 14 β -steroid (if the difference in size of the terminal ring is ignored). The contributions of the two cis-fused bicyclic components, being of opposite signs, tend to cancel out for the 5 β ,14 β -isomer, giving a small value of $\Delta\epsilon$. The corresponding trans-fused bicyclic systems are, by contrast, essentially

symmetrical about the shared C-C bond, except in respect of the size of ring D. Small values of $\Delta\epsilon$ are therefore observed for the 5 α ,14 α -hydrocarbons, and especially for D-homo-5 α ,14 α -androstande. The results for 5 α ,14 α - and 5 β ,14 α -cholestande suggest that the addition of the C₈ side-chain at C-17 makes relatively little difference to the observed c.d.

Saturated aliphatic molecules containing quaternary carbon atoms are known to show absorption of high intensity at 176 nm in hexane solution which may be ascribed to a $\sigma \rightarrow \sigma^*$ transition;⁷ therefore the observed dichroism of the steroid skeleton probably arises from the two quaternary atoms C₁₀ and C₁₃ or their associated bonds.

We thank the Science Research Council for a research grant (to Prof. Klyne).

C.d. of steroid hydrocarbons (in hexane) at the lowest wavelength measured

Androstandes:	5 α ,14 α	+0.4 (184 nm)	5 β ,14 α	+1.7 (183 nm)
	5 α ,14 β	-1.3 (184 nm)	5 β ,14 β	+0.6 (184 nm)
<u>D</u> -Homo-androstande:	5 α ,14 α	+0.1 (183 nm)		
Cholestandes:	5 α ,14 α	+0.5 (183 nm)	5 β ,14 α	+1.1 (184 nm)

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