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OPTICAL ACTIVITY IN CHIRAL OLEFINS

UV AND CD SPECTRA OF SOME TRITERPENOID HYDROCARBONS

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Abstract—The UV and CD spectra of several related mono unsaturated steroidal and triterpenoid hydrocarbons have been measured. The electronic assignments are discussed and it is found that the Scott-Wrixon Rules can be successful in correlating the sign of the circular dichroism with molecular structure.

Prompted by improved methods of measuring optical activity in the UV region and hence an improved analysis of the electronic absorption bands related to the π electrons of the double bond, several papers have recently appeared in the literature discussing the optical activity of chiral olefins. However, no definitive information is yet available concerning all the electronic states involved and many questions remain unanswered about their chiroptical properties.

In this paper are reported the UV and CD spectra of a series of mono olefinic triterpenoid hydrocarbons characteristic of primitive plants,[1-4] some other related mono unsaturated steroidal and triterpenoid hydrocarbons and 3β-hydroxycholest-8(14) ene. In general, they constitute a suitable series of structurally complex olefins in which the location of the double bond is well defined and few allowed conformations have to be considered in the interpretation of their CD spectra.

Besides allowing a correlation between CD signs and molecular structure, these compounds afford the opportunity of investigating two other important aspects. Firstly, as all the transitions appear to be generally red-shifted compared to simpler olefins, one can have a more precise idea of the number, nature and relative energy order of the observed transitions, particularly those associated with the first singlet electronic absorption envelope. Secondly, the relative signs of the various CD bands are important and should prove to be a critical test for any theory of optical activity.

EXPERIMENTAL

All compounds were obtained as reported in the references (see Table 1). Their purities were checked by GLC on two different columns.[19]

UV and CD measurements were carried out under nitrogen with n-heptane solutions at room temperature using a Cary 14 or a Jouan Dichrographe model CD 185 respectively.

RESULTS AND DISCUSSION

For ease of comparison and discussion the compounds have been classified into groups according to the position of the double bond (Table 1). Group IV contains a miscellaneous set of compounds with various positions of the double bond in the hydrocarbon skeleton, whilst Group V involves two triterpenes having 7-membered rings associated with the double bond. The members of Groups I-IV and VI may all be treated as formally conformationally non labile whilst those of Group V may have two conformations due to the flexibility of the 7-membered ring (Fig. 5).

In most cases the UV spectra are characterised by one large broad band whose max is in the region 210–190 nm. However, of probable equal diagnostic importance are the molar extinction coefficients which vary between 5000 and 12,000. In some cases (Fig. 3, IV 1 and 3; Fig. 5, V2) there appears to be two electric dipole allowed transitions which probably correlate with the results of Snyder and Clark.[20] On the other hand, the CD spectra indicate that there may be at least three observable electronic transitions, two of which are certainly associated with the first singlet electronic absorption band.

In ethylene,[21] the $\pi_x \rightarrow 3s$ ($N \rightarrow R$) Rydberg transition has been located at 57,700 cm^{-1}, an electric quadrupole allowed transition ($\pi_x \rightarrow \pi^*_y$ or $\pi_y \rightarrow \pi^*_x$) at 60,000 cm^{-1} and the $\pi_x \rightarrow \pi^*_x$ ($N \rightarrow V$) transition at 61,100 cm^{-1}. These transitions generally red shift with carbon substitution at the chromophore. Further to this Snyder and Clark[20] have observed that there may be two observable electric dipole allowed transitions, both polarised along the double bond, in a tetra substituted olefin. In bicyclohexylidene these are located at 48,000 cm^{-1} and 55,000 cm^{-1}; whilst one is probably the $\pi_x \rightarrow \pi^*_x$ transition the other remains unassigned. However, in more complex molecules this is not necessarily the energy order and there have been many various attempts, both experimental and theoretical[20-34] to discuss electronic assignments and chiroptical properties based on these ideas.

The question of electronic assignment can be aided by a simple comparison of the UV and CD spectra.[22,23] In this context of prime importance is the fact that strong UV maxima unambiguously locate the positions of electric dipole allowed transitions. Thus, if the first CD band appears to be associated with the low energy tail of the first singlet electronic UV envelope, it is the second transition, as for example in the compounds of Group III

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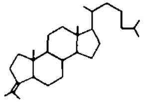
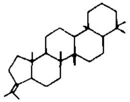
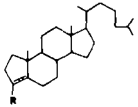
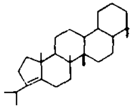
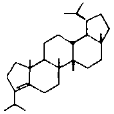
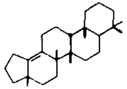
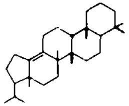
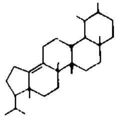
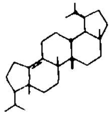
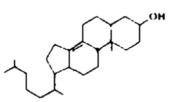
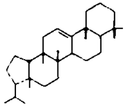
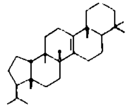
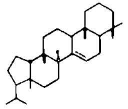
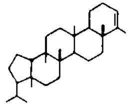
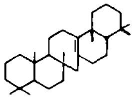
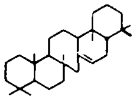
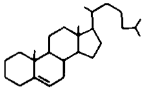
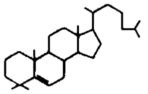
Table 1. Structures and spectral data

Group	Compound	Structure	UV	CD λ_{max}kK($\Delta\epsilon$); (prediction)†		
			λ_{max}kK($\epsilon \times 10^{-3}$)	Band I	Band II	Band III
Group I	3-Isopropylidene-A-norcholestane (I 1)[5]		51.0(10.6)	47.8(+6.3); (+)	53.5(−6.5); (−)	
Group I	A-Neogammacer-21-ene (I 2)[6]		51.0(10.6)	47.8(+5.0); (+)	54.0(−8.7); (−)	
Group II	A-Norcholest-3(5)-ene (II 1);[7] R = H		51.2(9.3)	49.4(−6.5); (−)	+; (+)	
Group II	3-Methyl-A-norcholest-3(5)-ene (II 2);[8] R = CH_3		50.5(9.7)	48.0(−9.9); (−)	+; (+)	
Group II	3-Isopropyl-A-norcholest-3(5)-ene (II 3);[9] R = $CH(CH_3)_2$		50.5(9.5)	47.7(−9.0); (−)	+; (+)	
Group II	A′-Neogammacer-17(21)-ene (II 4)[11]		51.9(7.9)	(See Fig. 2)		
Group II	A-Neolup-3(5)-ene (II 5)[12]		50.6(12.2)	47.7(−12.0); (−)	+; (+)	
Group III‡	22,29,30-Trisnor-B′ : A′-neogammacer-13(18)-ene (III 1)[13]		50.0(11.35)	45.5(+6.2); (+)	51.3(−6.5); (−)	
Group III‡	B′ : A′-Neogammacer-13(18)-ene (III 2)[14]		50.0(12.3)	45.4(+8.0); (+)	51.0(−9.2); (−)	
Group III‡	A : B-Neo-18,20βH-urs-9-ene (III 3)[10]		50.0(12.7)	45.4(+7.2); (+)	50.6(−6.1); (−)	
Group III‡	A : B-Neolup-9-ene (III 4)[10]		49.9(12.0)	45.5(+7.3); (+)	51.0(−10.0); (−)	54.0 (+)

	3β-Hydroxy-cholest-8(14)-ene (III 5)[15,§]			45.5(−7.7); (−)	49.5(+6.0); (+)	
Group IV	D:C-Friedo-B′:A′-neogammacer-9(11)-ene (IV 1)[16]		51.2(7.3)	48.0(−8.5); (−)	51.6(+2.7); (+)	54.0 (−)
	D:C-Friedo-B′:A′-neogammacer-8-ene (IV 2)[16]		50.2(8.1)	(See Fig. 3)		54.0 (+)
	D:C-Friedo-B′:A′-neogammacer-7-ene (IV 3)[16]		49.0(4.8) 54.0(6.4)	47.0(−7.5); (−)	+; (+)	
	D:A-Friedo-B′:A′-neogammacer-3-ene (IV 4)[16]		(See Fig. 3)	51.2(−1.0); (−)	+; (+)	
Group V	Isoserratene (V 1)[16]		49.1(7.2)	44.7(−2.0); (?)	47.9(+7.2); (?)	
	Serratene (V 2)[16]		48.4(5.4) 54.0(6.2)	48.0(−12.3); (?)	54.0(+14.3); (?)	
Group VI	Cholest-5-ene (VI 1)[17]		53.0(8.6)	49.8(+4.7); (+)	54.0(−16.0); (−)	
	4,4-Dimethyl-cholest-5-ene (VI 2)[18]		52.3(9.4)	(See Fig. 5)		

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†CD predictions are based on the sector rules suggested by Scott and Wrixon.[24]
‡In Group III CD predictions are based on B-ring configuration, those based on the "bulk" of the molecule violate the Scott-Wrixon Rules.
§Data taken from reference 24.

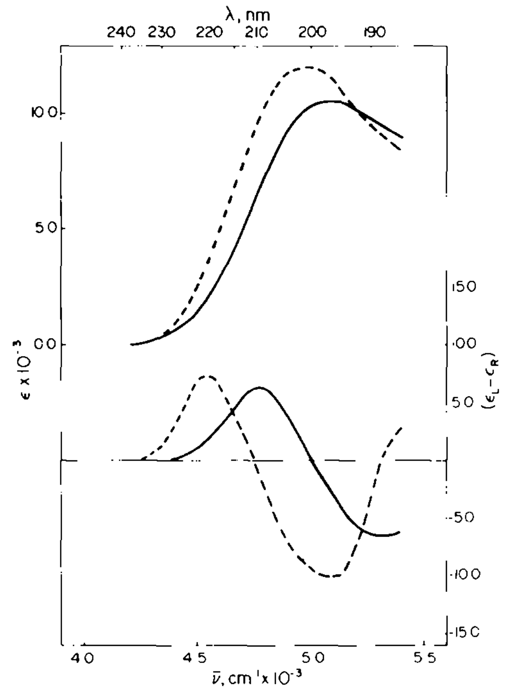

Fig. 1. ——, UV and CD spectra of I 1; – – –, UV and CD spectra of III 4.

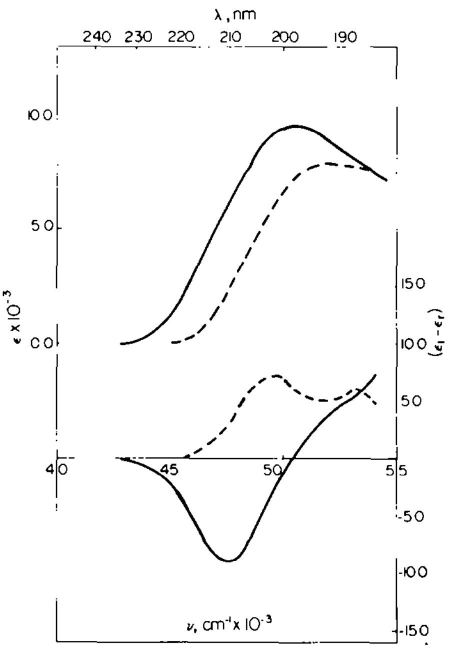

Fig. 2. ——, UV and CD spectra of II 3; – – –, UV and CD spectra of II 4.

(Fig. 1) which corresponds to the UV maximum and is, therefore, assignable as the $\pi_x \to \pi_x^*$ transition. In Group III the lowest energy transition is thus assignable as deriving from the electric quadrupole transition ($\pi_x \to \pi_y^*$ or $\pi_y \to \pi_x^*$) or the $\pi_x \to 3s$ transition. Unfortunately, this argument is not readily extendable to all the compounds described here as the UV maximum often corresponds to or nearly to a cross-over in the CD spectrum and overlapping transitions lead to uncertain amounts of cancellation.

To avoid this uncertainty the bands that are observable in the CD spectra are labelled (cf. Scott *et al.*[24]) according to their energy order.

Band I < Band II < Band III.

The signs of these bands, along with the sector rules required to predict them, are given in Table 1.

Scott and Wrixon[24] in their earlier papers on the optical activity of olefins suggested that Band I is assignable as the electric dipole allowed $\pi_x \to \pi_x^*$ transition obeying a +XYZ sector rule, although in later papers[24] prompted by the work of Fetizon and Hanna[25] it was suggested that Bands I and II may be near degenerate and that Band II may often mask Band I (or *vice versa*), thereby, accounting for any exceptions to the sector rules.

On the other hand, in a recent paper Yogev *et al.*[26] questioned this energy order and proposed that Band I is the magnetic dipole allowed $\pi_x \to \pi_y^*$ whilst Band II corresponds to the electric dipole allowed $\pi_x \to \pi_x^*$. As discussed previously the strict comparison of UV and CD spectra can assist in resolving this dilemma. However, the octant rules proposed by Scott and Wrixon[24] are seen to be obeyed with the mutual opposite signs of Bands I and II always being preserved except possibly in compounds II 4 and IV 2 (Figs. 2 and 3) although these two exceptions may be reconcilable by the possible masking effects. This consistency of relative signs is a fundamental requirement if a simple first order static field theory is to be invoked to account for the optical activity in an olefin chromophore. These concepts are clearly demonstrated by the spectra of Groups I and III (Fig. 1), within the latter group the opposite sign of cholest 8(14)-en-3-β-ol (III-5) compared to the other members of the group can readily be accounted for by an octant rule.

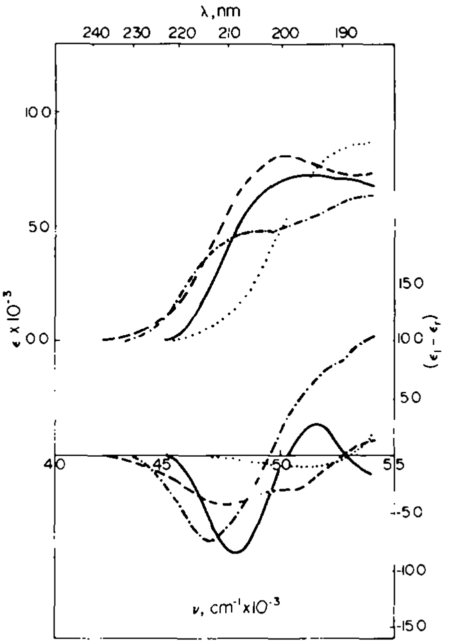

Fig. 3. ——, UV and CD spectra of IV 1; – – –, UV and CD spectra of IV 2; –·–·–·, UV and CD spectra of IV 3; · · · · · ·, UV and CD spectra of IV 4.

In Group II, compounds II 1, 2 and 3 show very similar spectra with the difference in the UV between II 1 and II 2 being probably related to the methyl group associated with the chromophore in the latter compound.[21] However, II 4 (Fig. 2) appears to be quite anomalous and the electronic assignments are uncertain, it may well be that Band II is observed as a trough in the positive Band I, this would certainly be consistent with the octant rules. The only structural feature that distinguishes II 4 from the other members of Group II is the appearance of two 1,3 diaxial methyl interactions which must, therefore, transmit a different strain pattern.

The spectra of Group IV (Fig. 3) demonstrate clearly the dramatic variation in the UV and CD that can occur as the double bond is located at different positions in the neo-γ-cerane backbone, thereby, manifesting the influence of the environment on the olefin chromophore. The environment of the double bond in IV 4 is very different from that of the other olefins, because it is located in only one ring and is therefore possibly the least strained. Accordingly, its UV[21] and CD[27] spectra are similar to those exhibited by open chain olefins.

Group VI (Fig. 4) affords an example of the effect described by Fétizon *et al.*,[24,25] i.e. the masking of Band I by Band II. In compound VI 1, two CD bands are clearly seen whilst in VI 2 the first having apparently blue shifted, is hidden under the second. This is also manifest in the UV spectra with VI 2 showing an increase in the ϵ_{max} as opposed to a decrease in the intensity of the tail. This leads to the conclusion that the second CD band in cholest-5-enes is associated with the UV maximum and assignable as the $\pi_x \rightarrow \pi_x^*$ transition in accord with Yogev *et al.*[26] but not Scott *et al.*[24] It is interesting to note that the effect of 4-dimethylation can be interpreted simply in terms of a blue shift of Band I with the $\pi_x \rightarrow \pi_x^*$ transition remaining unchanged.

The data reported here support and extend the ideas of Scott *et al.*[24] There are now seen to be three singlet electronic transitions associated with the olefin chromophore although in many cases this is not apparent due either to overlapping transitions or the probability of transitions occurring outside the range of present commercial spectrometers (i.e. beyond 185 nm). Numerating these transitions and applying octant rules as described by Scott *et al.*[24] has proved successful in correlating optical activity and molecular structure. It has further been shown that comparison of UV and CD data can assist in making electronic assignments. However, it is clear that further studies[34] (low temperature spectra and vacuum UV measurements) are necessary before sure electronic assignments can be made permitting a more complete correlation between UV spectra, CD spectra and molecular structure.

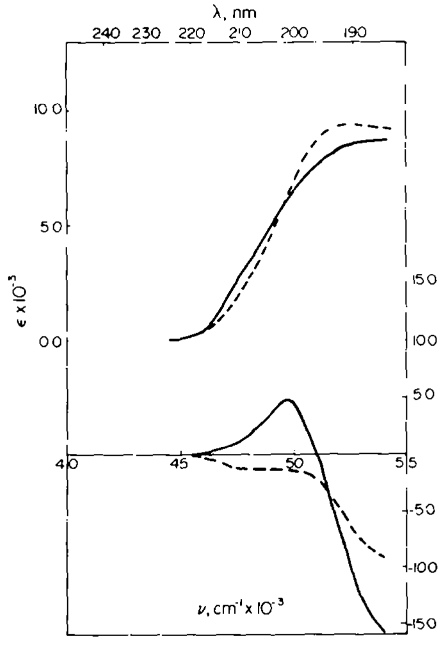

Fig. 4. ——, UV and CD spectra of VI 1; - - -, UV and CD spectra of VI 2.

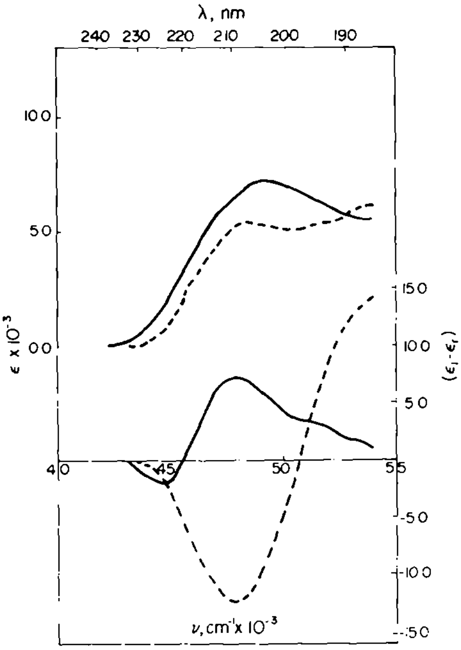

Fig. 5. ——, UV and CD spectra of V 1; - - -, UV and CD spectra of V 2.

Despite these uncertainties it has been demonstrated that a correlation between the relative energies of the various CD bands, their signs and the UV spectra (both λ_{max}'s and extinction coefficient) should eventually afford a means of estimating the amount and type of stress and strain in an ethylenic bond along with other structural information.

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