Assignment of the First Singlet Electronic Circular Dichrosim Band in the Olefin Chromophore

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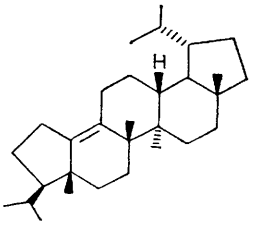
Summary The first of three singlet electronic transitions associated with the double bond of a mono-olefin is assigned as the $\pi_x \rightarrow 3s$ Rydberg transition on the basis of far and vacuum u.v. absorption and c.d. measurements at ambient and low temperatures.

THE lowest energy observable singlet electronic c.d. band in simple chiral mono-olefinic hydrocarbons[1,2] such as α-pinene can, at least in the gas phase, be assigned as the $\pi_x \rightarrow 3s$ Rydberg transition associated with the ethylenic chromophore. More complex mono-olefins including steroids and triterpenes have now been studied, with the result that again the $\pi_x \rightarrow 3s$ Rydberg transition is seen to play an important role in the optical activity observed in the 45,000—54,000 cm^{-1} region.



(I)

The $\pi_x \rightarrow 3s$ Rydberg transition in chiral olefins can be assigned on the basis of three criteria.[1-3] It is pressure-sensitive, being blue-shifted at higher pressures or in media of high 'internal pressure' (*e.g.* solutions at low temperatures); it is capable of possessing a relatively large dissymmetry factor; and the vibronic structure characterising the 3*s* excited Rydberg state (spacings of *ca.* 1350 cm^{-1}) corresponds to single quanta of the totally symmetric C=C stretching vibration. These are precisely the properties exhibited by the first singlet electronic c.d. band of several steroidal and triterpenoid mono-olefins that have now been studied. On this basis this transition may therefore be assigned as the $\pi_x \rightarrow 3s$ Rydberg transition. An example is presented here.

The spectra of A : B-neolup-9-ene (I) (Figure) clearly show that at low temperatures whilst the second c.d. band, negative in sign, remains relatively unchanged at *ca.* 50,000—51,000 cm^{-1} (*cf.* u.v. maxima) the first, positive c.d. band is blue shifted from 45,000 to 48,000 cm^{-1} and a distinct vibronic structure exhibiting 1350 cm^{-1} spacings is developed in both the c.d. and the isotropic absorption. The observed blue-shift at low temperatures is much less marked than in simpler olefins; perhaps the more complex structures involved here either 'stabilise' the Rydberg state or 'protect' the chromophore from the solvent.

It has been recognised that the first singlet electronic absorption band of steroidal mono-olefins is an envelope of

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two transitions.[4,5] Scott and Wrixon[4] have assigned the lower energy one as $\pi_x \rightarrow \pi_x{}^*$ and the higher energy one $\pi_x \rightarrow \pi_y{}^*$. Reverse assignments however were made by Yogev *et al.*[5] The present work now indicates that the first c.d. band may, in fact, be the $\pi_x \rightarrow 3s$ Rydberg transition which, being nominally polarised out of the C=C plane, affords a basis for the findings of Yogev *et al.*[5] with steroidal olefins in stretched films.

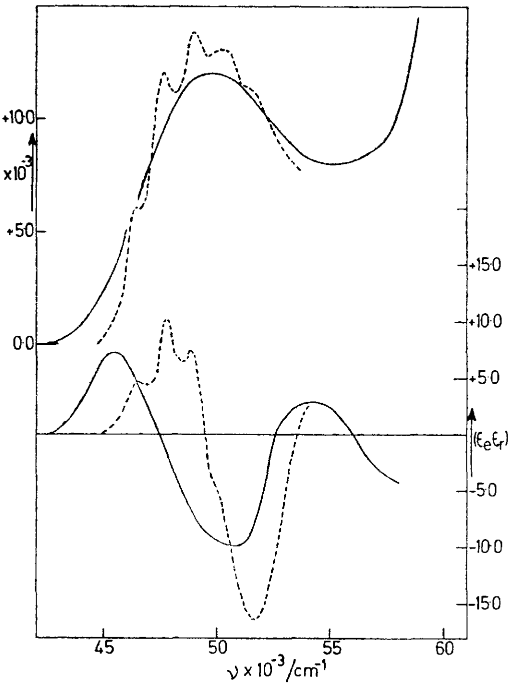

FIGURE. The u.v. and c.d. spectra of A:B-neolup-9-ene (I) in 3-methylpentane and/or n-pentane: ———— at 296 K; - - - - at 80 K.

Further, the position of the Rydberg transition with respect to the second transition may vary considerably (*cf.* this work with that of Drake and Mason[1]), thus explaining the uncertainty of assignment and the mutual masking effects of the two transitions illustrated by Fétizon *et al.*[6]

Following this Rydberg transition there appears in the c.d. spectra a bisignate 'couplet' of transitions (*ca.* 51,000 and 54,000 cm^{-1}) analogous to those described by Andersen and Ohta.[7] The lower-energy component, negative in sign, may be assigned as the $\pi_x \rightarrow \pi_x{}^*$ transition on the basis of its correlation with the isotropic absorption maximum. The higher-energy component, positive in sign and reduced in intensity owing to overlap with the onset of hydrocarbon-backbone c.d. of opposite sign,[8] is assignable as deriving from a formally magnetic dipole-allowed, electric-dipole forbidden transition ($\pi_x \rightarrow \pi_y{}^*$ or $\pi_y \rightarrow \pi_x{}^*$) in accord with the suggestions of Mason and Schnepp.[2]

Spectra in the region 40,000—54,000 cm^{-1} were measured with a Cary 17 or a Jouan CD 185 spectrometer; measurements were repeated and extended to 60,000 cm^{-1} on a vacuum u.v.–c.d. spectrometer[9] constructed at King's College, London.

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