Optical Activity of the Olefin Rydberg Transition

By Alex F. Drake and Stephen F. Mason*

(*Department of Chemistry, King's College, Strand, London* WC2R 2LS)

Summary A Rydberg Cotton effect of chiral olefins (exemplified by α-pinene) is characterised by the vibronic structure in the gas-phase c.d. spectrum and a marked blue-shift with increase of solvent density.

Studies of the Cotton effects of chiral alkenes centre on the electric-dipole $\pi_z \rightarrow \pi_z{}^*$ olefin transition near 50 kK for which an octant rule[1] and an allylic axial hydrogen rule[2] have been suggested. A higher-energy magnetic-dipole transition, $\pi_x \rightarrow \pi_y{}^*$ or $\pi_y \rightarrow \pi_x{}^*$, detected near 60 kK in the electron-impact spectrum of ethylene,[3] helps to account for the apparent exceptions to the octant rule[4] and provides theoretically the complementary excitation required to produce with the $\pi_x \rightarrow \pi_x{}^*$ transition the major rotational strengths of the chiral olefin chromophore.[5-7] Calculations indicate[5,6] that the lower-energy Rydberg transition, $\pi_x \rightarrow 3s$, is expected to have a minor rotational strength of the same sign as that of the $\pi_x \rightarrow \pi_x{}^*$ transition.

We find that (−)-α-pinene (Figure) and other chiral olefins in the vapour phase give a sharp Rydberg c.d. band near 45 kK with an appreciable rotational strength of opposite sign to that of the 50 kK c.d. band. The sharp 45 kK c.d. band is ascribed to a Rydberg transition on the grounds of a 1350 cm^{-1} vibronic spacing,[8] a broadening of the vibronic structure, and a blue-shift with an increase of inert gas pressure[9] and, more particularly, with an increase of solvent density.[8,10] The olefin Rydberg 3*s* orbital has a radial electron-density maximum 2·1 Å from the centre of the chromophore and it is destabilised by an increase in the density of the solvation shell.[8] Thus the Rydberg cd.band of (—)-α-pinene at 45 kK in the gas phase shifts to 49 kK in 3-methylpentane at ambient temperature (D_{15} = 0·669), becomes a shoulder at 50·5 and then *ca.* 52 kK in that solvent at —95 and —182°, respectively, (D_{-182} = 0·82), and merges into the higher-energy positive c.d. band system >54 kK in 2,2,2-trifluoroethanol (D_{20} = 1·468) (Figure).

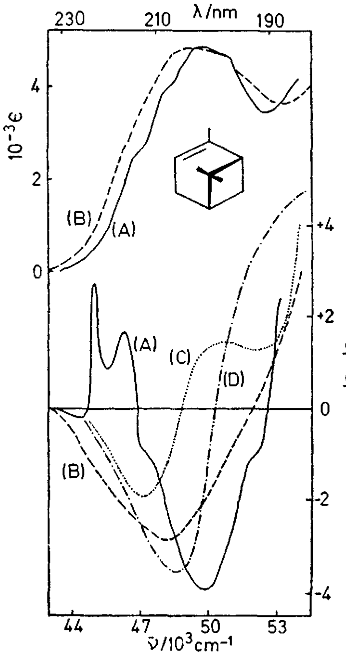

FIGURE. *The electronic spectrum (upper curves) and c.d. (lower curves) of* (—)-*α-pinene* (A) *in the gas phase,* (B) *in* 2,2,2-*trifluoroethanol, and in* 3-*methylpentane* (C) *at* —95° *and* (D) *at* —182°.

The absorption band of (—)-α-pinene shows a red-shift on changing from the vapour phase to solution, like the negative $\pi_x \rightarrow \pi_x{}^*$ c.d. band near 50 kK (Figure), indicating that the Rydberg $\pi_x \rightarrow 3s$ transition makes only a small contribution to the isotropic absorption. The dissymmetry factor, $g = (\Delta\epsilon/\epsilon)$, of the Rydberg transition is therefore large, possibly *ca.* 10^{-2}, relative to that (6×10^{-4}) of the $\pi_x \rightarrow \pi_x{}^*$ transition. Torsion of the π-bond and substituent-induced mixing with the $\pi_x \rightarrow \pi_y{}^*$ excitation give the $\pi_x \rightarrow \pi_x{}^*$ transition rotational strengths of opposite sign, the resultant being smaller than either of the individual contributions.[7] The large *g*-factor suggests that the Rydberg transition derives rotational strength from one main source, probably π-bond torsion, since the $\pi_x \rightarrow 3s$ upper state has an equilibrium torsion angle[8] of 25° and the observed 0–0 vibronic band at 44·9 kK is stronger than the 0–1 at 46·25 kK (Figure).

The large Rydberg *g*-factor indicates that caution is required in the application of sector rules to the c.d. spectra of chiral olefins if based on the assumption that only two Cotton effects are present in the 45—54 kK region, due to the $\pi_x \rightarrow \pi_x{}^*$ and the $\pi_x \rightarrow \pi_y{}^*$ or $\pi_y \rightarrow \pi_x{}^*$ transition. However, the Rydberg Cotton effect is detectable even in non-volatile chiral alkenes through the marked blue-shift observed on changing from a paraffin to a perfluoroalcohol solvent.

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