Solvent Effects in Olefin Circular Dichroism

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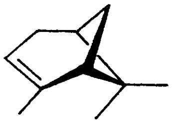
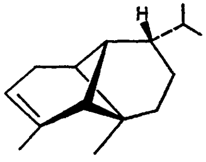
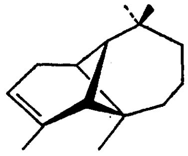
Summary The c.d. spectra of olefins, contrary to a recent report, are not subject to notable shifts due to solvent density and the shifts observed in perfluoroalcohols should be interpreted with great caution owing to the ready isomerization of olefins in these solvents.

THE c.d. of chiral olefins has been investigated in our[1] and other laboratories[2] and a number of theoretical and practical features are still controversial. We recently presented our evidence for assigning the c.d. couplet observed for many systems to a coupling of the $\pi_x \rightarrow \pi_x^*$ and $\pi_x \rightarrow \pi_y^*$ transitions.[3] The lower-energy $\pi_x \rightarrow 3s$ transition, expected to have minor rotational strength,[4] has been implicated in the solvent-dependent c.d. spectrum observed for α-pinene.[5] The appearance, in the gas-phase spectrum, of a previously unobserved band (centred at 220 nm) of opposite sense to that seen in solution, which displayed the expected vibronic spacing was central to this work. It was suggested that this assignment was confirmed by the observation of a blue-shift on transfer to an inert solvent and a further blue-shift on cooling or transfer to perfluoroalcohol solvents. Although we do not disagree with the assignment Drake and Mason accord to the band observed in the gas phase, we now present data which suggest that the 'blue-shift' is not associated with solvent density. Furthermore the two common classes of olefin c.d.: torsion couplets and strong apparent singlets (which we attribute to the reinforcing combination of the lower energy portion of the torsion couplet with the rotatory contribution of the $\sigma_a \rightarrow \pi_x^*$ transition)[3] are essentially unaffected by solvent density and polarity.


(I)


(II)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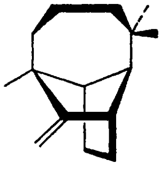
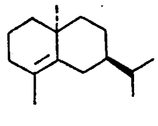

(IV)


(V)

The c.d. of (—)-α-pinene (I) (and its prenylogues) in a wider variety of solvents was particularly informative (see Figure). The spectrum in pentane (d_{20} 0·626) is superimposable with that reported for cyclohexane (d_{20} 0·78) solution by Scott and Wrixon.[2] Of the prenylogues, (—)-α-copaene (II) displays a very similar spectrum in pentane; however (—)-α-longipinene (III) has an enhanced positive band at *ca.* 205 nm, corresponding to the position of the $\pi_x \rightarrow 3s$ band of Drake and Mason in alkane solvents.[5] In CF_3CH_2OH (d_{20} 1·46) a negative c.d. band ($\Delta\epsilon_{210}$ −2·9) appears in this region† (presumably due to the blue-shift of the $\pi_x \rightarrow 3s$ band) and hexafluoropropan-2-ol (HFIP, d_{20} 1·61) produces an even stronger negative band ($\Delta\epsilon_{209}$ −4·7). We were unable to obtain reliable data for α-copaene in fluoro alcohols owing to a very rapid fragmentation promoted by these acidic non-nucleophilic solvents.‡ However, the negative band of α-longipinene appeared in the HFIP spectrum.

Owing to the unusual solvent properties of HFIP, we extended the series to MeCN (d_{20} 0·78), 95% aq. EtOH (d_{20} 0·80), and perfluoroheptane (d_{20} 1·76) in order to distinguish between polarity and density effects. For α-pinene and longipinene the spectra in perfluoroheptane resemble those in pentane rather than HFIP: clearly the dramatic changes associated with fluoro-alcohol solvents cannot be attributed to solvent density alone. Although other correlations suggest that the maximum or inflection at 202—215 nm in all solvents except the fluoro-alcohols is due to the transition observed at *ca.* 221 nm in the gas phase this is not established with certainty.

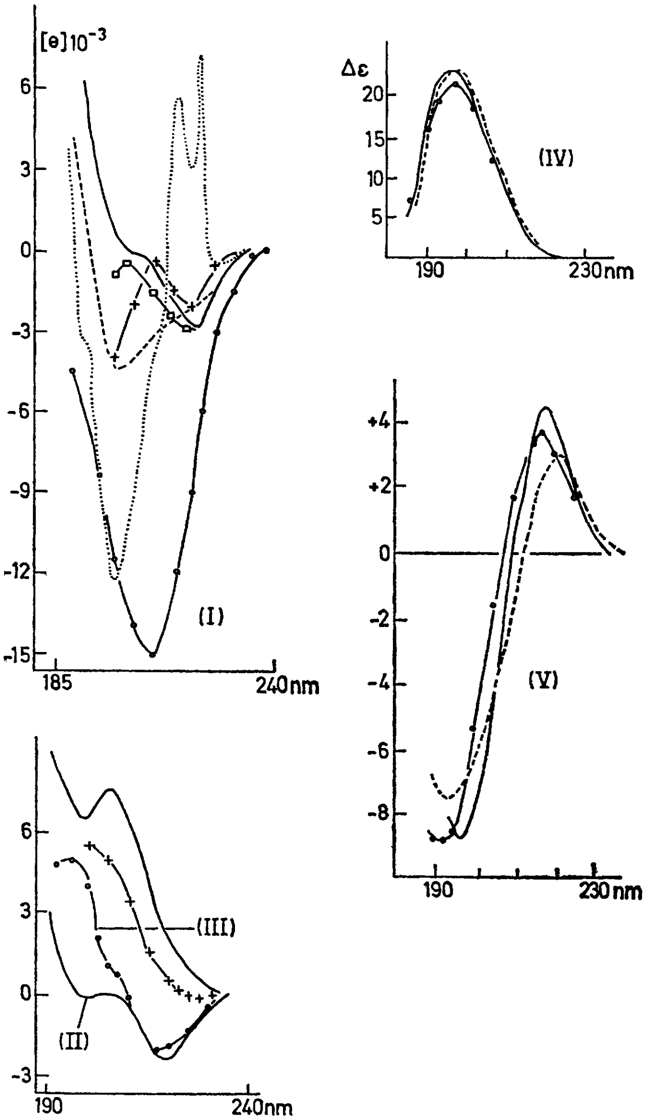


FIGURE. The c.d. spectra (linear in nm) of compounds (I)—(V) in a variety of solvents: ......, gas phase; ———, n-C_5H_{12}; ----, MeCN; -+-+-, C_7F_{16}; -□-□-, 95% EtOH; -○-○-, $(CF_3)_2CHOH$. In the case of (II) only the spectrum in pentane is shown; the additional traces are of (III) in C_7F_{16} and HFIP.

The major solvent dependence of the c.d. spectra of pinenes is not typical of chiral olefins, the data for longi-

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† Our data in CF_3CH_2OH are not shown in the Figure since they correspond within experimental error, to those reported previously.[5]

‡ The use of HFIP (and CF_3CH_2OH) for olefin c.d. studies requires particular care since many olefins isomerize when kept in these solvents. It is essential to take spectra rapidly and to assay for olefin purity immediately afterward: α-pinene has a half-life of *ca.* 4 h in HFIP.

folene and 10-*epi*-eudesm-4-ene being typical for strong olefin Cotton effects and couplets. The only generalization arising from our studies is a blue-shift of the high energy portion of couplets in polar solvents.

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