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THE ABSORPTION AND CIRCULAR DICHROISM SPECTRA OF CHIRAL OLEFINS

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Abstract—Absorption and CD spectra over the quartz and vacuum UV region down to 165 nm are reported for a range of chiral alkenes in the vapour phase and in solution from +70° to −185°C. A major couplet of oppositely-signed CD bands with comparable band areas, near 48 and 55 kK, is observed in a number of dissymmetric olefins and in some cases a weaker Rydberg CD absorption is found at lower frequency. The Rydberg CD band is characterised by its sharp vibronic structure in the vapour phase and by large blue-shifts produced on passing to the condensed phase and by a reduction in temperature. The olefin couplet of major CD bands with opposite sign is assigned to a near-complete mixing of the electric-dipole $\pi_x \rightarrow \pi_x^*$ and the magnetic-dipole $\pi_x \rightarrow \pi_y^*$ excitations, producing a pair of isotropic absorption bands with the same polarisation and comparable dipole strengths associated with the CD couplet. Three mixing mechanisms are discussed; sterically-induced π-bond torsion, a first-order static field model, and a second-order dynamic-coupling model dependent, respectively, upon the effective charge and upon the mean polarisability of dissymmetrically-located substituent. The latter two models give the octant rule previously proposed empirically connecting the sign of the rotational strength of the lower- and higher-frequency member of the olefin CD couplet with the position of the substituent in the chromophore coordinate frame.

INTRODUCTION

Studies of the Cotton effects of chiral alkenes have been confined largely to the quartz ultraviolet region ($\lambda >$ 185 nm) and generally they cover only the first or the first two CD bands in the spectrum.[1-13] The octant rule +XYZ (Fig. 1) connecting the position of a substituent in the coordinate frame of the olefin chromophore with the sign of the lowest-frequency Cotton effect induced by the substitution has been proposed, the Cotton effect being assigned to the $\pi_x \rightarrow \pi_x^*$ olefin transition.[3-5] A number of exceptions to this octant rule have been observed[6-9] and these are ascribed to an overlying stronger CD absorption of opposite sign at higher frequencies, discernable by Gaussian analysis,[4] or to the anti-octant effect of the hydroxyl group and other oxygen-containing substituents.[5] Alternatively the Cotton effects of chiral alkenes observable in the quartz UV region are attributed to the transformation of the symmetric olefin group into an inherently dissymmetric chromophore by substitution, either through an interaction with allylic axial C–H bonds[2] or by π-bond torsion,[10] as theoretical studies suggested.[14-16]

The pioneer vacuum UV studies of the CD spectra of chiral alkenes in the vapour phase by Schnepp *et al.*[17,18] indicate that the analysis of the optical activity of dissymmetric olefins based solely on quartz UV solution data is necessarily limited, as do vapour-phase CD measurements in the latter region.[12] Accordingly we have assembled a CD spectrometer for the vacuum UV region following previous designs,[19-21] and report here CD measurements of chiral alkenes in the vapour phase and in solution down to 165 nm, together with earlier measurements[12] limited to 185 nm.

The lowest-energy olefin Rydberg transition

In the spectrum of ethylene two singlet electronic transitions have been observed[22,22] at a lower energy than the electric dipole allowed $\pi_x \rightarrow \pi_x^*$ excitation at 61.7 kK, firstly, an electric quadrupole transition, which lies only 1200 cm^{-1} lower in frequency[24] and, secondly, the Rydberg transition,[25] $\pi_x \rightarrow 3s$ (Fig. 1), which is weakly electric-dipole allowed and lies some 3600 cm^{-1} below the $\pi_x \rightarrow \pi_x^*$ excitation. The absorption due to a Rydberg transition of an olefin in the gas phase at low pressure is characterised by sharp vibronic bands with a spacing of some 1350 cm^{-1}. On increasing the pressure by the addition of an inert gas to ~ 10^2 atmospheres the vibronic structure is broadened and the Rydberg band system as a whole shifts to higher frequencies.[22,23,26] The olefin 3s united-atom orbital is large, with a radial electron-density maximum at 2.1 Å from the centre of the chromophore,[22] and the Rydberg excited state is progressively destabilised by an increasing pressure of environmental inert-gas molecules.[23,26] In solution, the vibronic structure of the olefin $\pi_x \rightarrow 3s$ Rydberg transition is lost and the band undergoes further and often substantial blue-shifts which appear to correlate with the effective internal pressure of the solvent. At ambient temperature the cohesive internal pressure of paraffin solvents is some 10^3 atmospheres, while that of alcohols and other hydrogen-bonded solvents is larger, ~10^4 atmospheres, and the internal pressure of all liquids increases on cooling.[27] The internal pressures of heptane and of ethanol increase by some 20% on reducing the temperature from 50° to 0°C.[27]

The vapour-phase CD spectra of (−)-α-pinene **1**, (+)-camphene **2**, and (−)-bornene **3** show sharply-structured bands at low frequency, 44–49 kK, with a spacing of 1400 cm^{-1} in the former two cases (Figs. 2–4). In a paraffin or alcohol solution at ambient or at low temperature the vibronic structure is lost and the Rydberg band undergoes a large blue-shift, or disappears. In 3-methylpentane solution at −95°C the Rydberg CD band of **1** shifts, relative to the corresponding gas-phase absorption, some 4000 cm^{-1} to higher frequency, showing a further blue-shift of ~2000 cm^{-1} on cooling to −182°C, so that the Rydberg band becomes a shoulder on the more intense positive CD absorption at higher frequency (Fig. 2). With **1** in trifluoroethanol solution at ambient temperature the latter CD absorption presumably overlies the Rydberg CD band, now shifted to the blue by more than 7000 cm^{-1} (Fig. 2).

The Rydberg absorption of (+)-camphene **2**, represen-

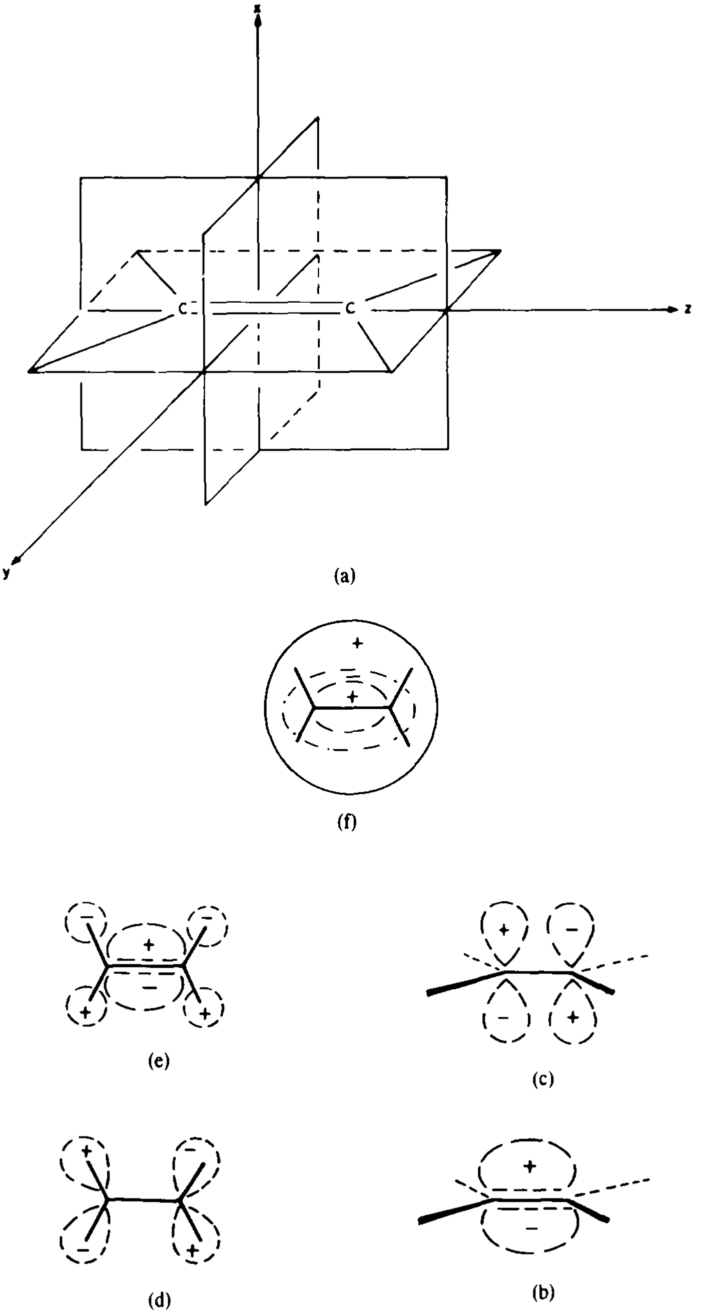
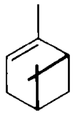


Fig. 1. The olefin chromophore; (a) the coordinate frame, (b) the π_x orbital, (c) the π_x^* orbital, (d) the π_y orbital, (e) the π_y^* orbital and (f) the Rydberg united-atom 3s orbital.

ted by the negative CD band at 45 kK in the gas-phase spectrum, disappears in 3-methylpentane solution where the Rydberg CD band is manifest only by the trough, observed near 47 kK at 20°C and near 49 kK at −100°C, in the strong positive CD absorption, rising to higher frequencies (Fig. 3). Similarly the positive Rydberg CD band of (−)-bornene 3, at 48.2 kK in the gas phase spectrum, disappears in the corresponding solution CD spectra, being represented solely by the shoulder near 50 kK on the strong negative CD absorption observed at 20° or 60°C (Fig. 4). No trace of the Rydberg CD band remains in the solution CD spectrum of 3 measured at either −100° or −182°C (Fig. 4).

In contrast neither the gas-phase nor the solution CD spectra of (−)-β-pinene(4) exhibit the features distinctive of a Rydberg band (Fig. 5). Similarly the olefin $\pi_x \rightarrow 3s$ Rydberg bands are not prominent in the absorption and CD spectra of (+)-*trans*-cyclooctene, although shoulders on the low-frequency side of the $\pi_x \rightarrow \pi_x^*$ CD and isotropic absorption band are attributed to the Rydberg transition.[17] In these cases the rotational strength of the Rydberg $\pi_x \rightarrow 3s$ excitation and the adjacent $\pi_x \rightarrow \pi_x^*$ or other valence-state transition have the same sign and the intrinsically weaker Rydberg absorption is not evident in the experimental CD spectra. When the Rydberg and the adjacent valence state transition have rotational strengths



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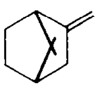

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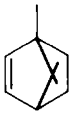

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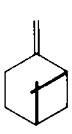

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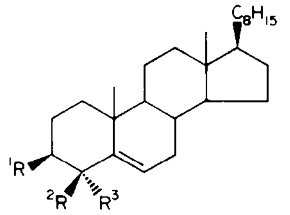
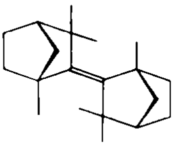


5: R^1 = R^2 = R^3 = H
6: R^1 = R^2 = H, R^3 = OH
7: R^1 = R^3 = H, R^2 = OH
8: R^1 = OH, R^2 = R^3 = H
9: R^1 = H, R^2 = R^3 = Me



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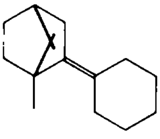

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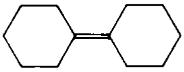

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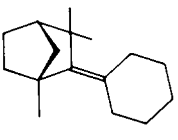

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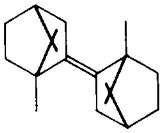

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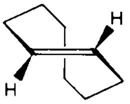

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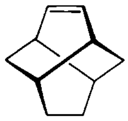

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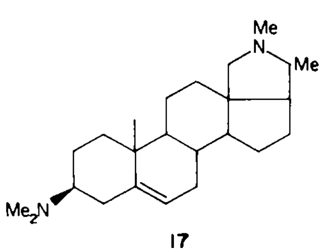

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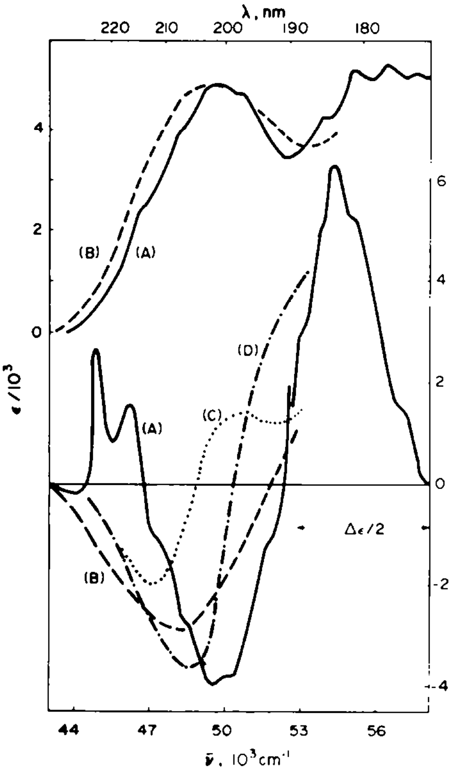

Fig. 2. The absorption spectra (upper curves) and CD spectra (lower curves) of (−)-α-pinene 1 (A) in the vapour phase, (B) in 2,2,2-trifluoroethanol, and in 3-methylpentane, (C) at −95° and (D) at −182°C.

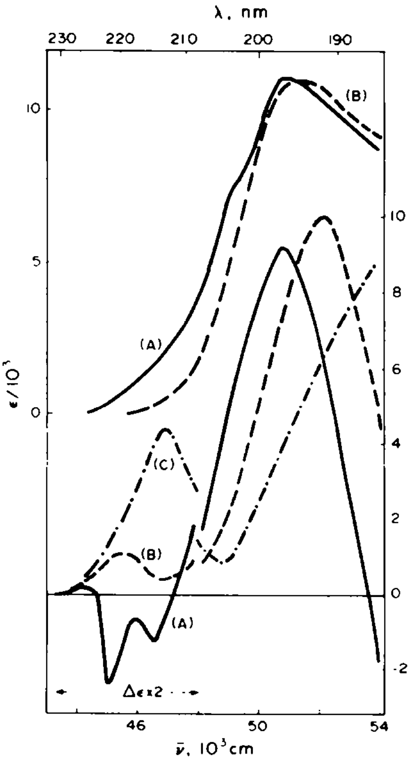

Fig. 3. The absorption spectra (upper curves) and CD spectra (lower curves) of (+)-camphene 2, (A) in the gas phase, and in 3-methylpentane, (B) at +20° and (C) at −100°C.

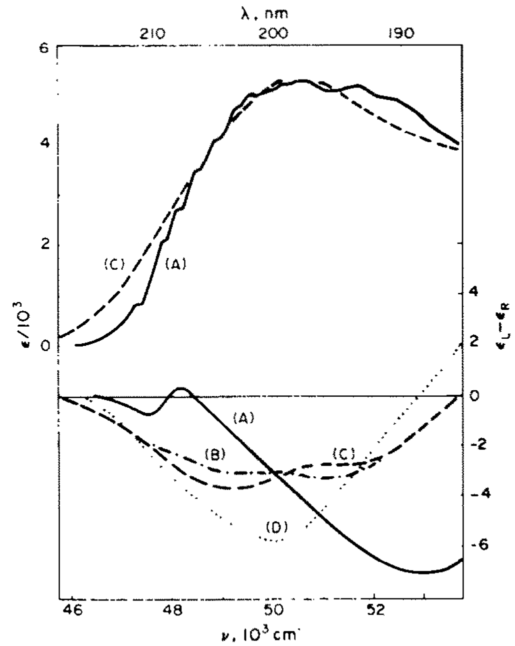

Fig. 4. The absorption spectra (upper curves) and CD spectra (lower curves) of (−)-bornene **3**, (A) in the gas phase, and in *iso*-octane, (B) at +60° and (C) +20°, and (D) in 3-methylpentane at −100° and at −182°C.

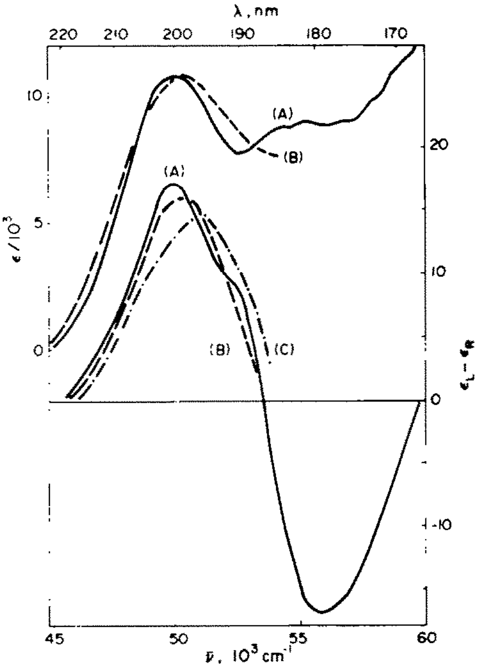

Fig. 5. The absorption spectra (upper curves) and CD spectra (lower curves) of (−)-β-pinene **4**, (A) in the vapour phase, and in 3-methylpentane (B) at +20° and (C) at −100°C.

of opposite sign the weaker Rydberg absorption is more readily detected and characterised in the gas-phase and in the solution CD spectra (Figs. 2–4). From the study of the CD spectra of the volatile olefins **1–4**, and previous CD studies of olefins in the gas phase,[12,17,18] it is concluded that there is no necessary relationship between the signs of the rotational strength of the olefin Rydberg $\pi_x \to 3s$ excitation and that of the adjacent valence shell transition. These olefin transitions may give rise to two CD bands of opposite sign or of the same sign in the quartz UV region, and in the former case stereochemical conclusions based on the assumption that the lowest energy CD band has a valence shell origin may be vitiated.

The majority of chiral alkenes studied hitherto, notably the steroidal olefins, are insufficiently volatile to permit vapour-phase CD measurements, where the sharp structured Rydberg absorption is evident. However, the Rydberg CD band in solution may be characterised, although less completely, by the pronounced blue-shift observed on cooling and by its weakness relative to the valence-shell CD absorption. These criteria suggest that the lowest-energy CD band of Δ^5-cholestene **5** is Rydberg in character (Fig. 6). The minor positive CD band of **5**, lying at a frequency, 47 kK in paraffin solution at +70°C, where the isotropic absorption is not large, blue-shifts progressively through $4700\ \text{cm}^{-1}$ as the temperature is reduced to −190°C (Fig. 6). The major negative CD band of **5** is less temperature-sensitive and at low temperatures it begins to appear at the lower frequency (Fig. 6). Measurements of the CD spectrum of **5** at a single low temperature might suggest the presence of three discrete CD bands in the 45–55 kK region, due to three distinct electronic transitions, but the temperature-variation of the CD spectrum indicates that there are only two excitations, the one at lower energy being Rydberg in nature (Fig. 6).

These conclusions are supported by the linear dichroism (LD) spectrum of Δ^5-cholestene **5**, in a stretched polyethylene film over the 45 to 55 kK region.[28] The absorption ratio ($\epsilon_{\parallel}/\epsilon_{\perp}$) for radiation polarised parallel to that polarised perpendicular to the stretch-direction falls between the stationary values of 1.14 at 48 kK and 0.82 at

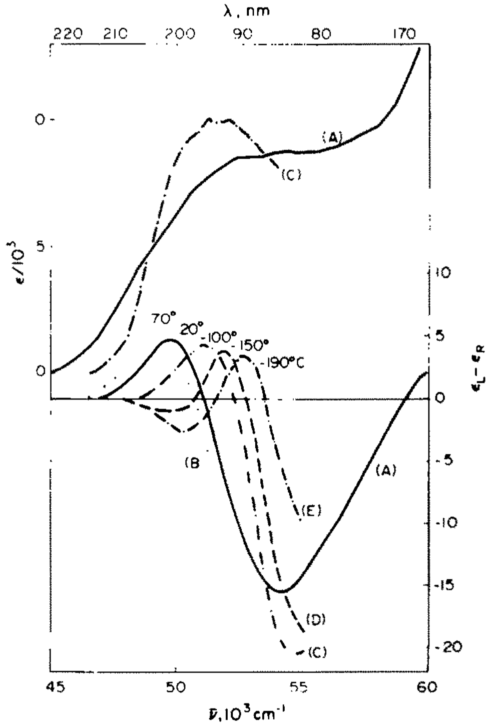

Fig. 6. The absorption spectra (upper curves) and CD spectra (lower curves) of Δ^5-cholestene **5**, (A) in n-pentane at +20°, (B) in *iso*-octane at +70°, and in 3-methylpentane, (C) at −100°, (D) at −150° and (E) at −190°C.

53 kK, from which the total isotropic absorption is resolved into two polarised bands.[28] The higher-intensity band at 54 kK is strictly z-polarised along the direction of the C=C bond, suggesting that it arises from the valence-shell $\pi_x \rightarrow \pi_x^*$ transition, whereas the lower intensity band at 49.5 kK has x-, y- and z-polarised moments (Fig. 1) in the ratio,[28] 24 : 17 : 96. These LD band maxima correspond to the CD band maxima observed for paraffin solutions of **5** at ambient temperature (Fig. 6). The Rydberg $\pi_x \rightarrow 3s$ transition in ethylene is x-polarised, perpendicular to the molecular plane,[22,23] but the corresponding transition in an unsymmetrically-substituted olefin, such as **5**, is expected to have a minor in-plane moment. Much of the z-polarised moment observed[28] in the Rydberg region 47–51 kK of the stretched-film LD spectrum of **5** derives from the low-energy tail of the z-polarised $\pi_x \rightarrow \pi_x^*$ transition, since at low temperature, where the positive Rydberg CD band is substantially shifted to higher frequencies, the onset of the isotropic absorption of **5** and that of the major negative CD band due to the $\pi_x \rightarrow \pi_x^*$ transition are virtually coincident (Fig. 6).

The CD spectra of 4α-hydroxy-cholest-5-ene **6** (Fig. 7), and of the 4β-hydroxy-, **7**, 3β-hydroxy-, **8**, and 4,4-dimethyl-derivative **9** of Δ^5-cholestene (Fig. 8) have the same basic form as that of the parent olefin **5** (Fig. 6). The CD spectrum of **6** at ambient temperature (Fig. 7), like that of **5** at low temperature (Fig. 6), might suggest the presence of three electronic transitions in the 46–54 kK region, but again the temperature-variation of the CD spectrum of **6** indicates (Fig. 7) contributions from only two excitations, the temperature-sensitive Rydberg transition near 50 kK with a minor positive rotational strength and the valence-shell transition with a major negative rotational strength, having an onset near 46 kK and a maximum beyond 54 kK. The CD spectra of **7**, **8** and **9** similarly suggest the provision of a minor positive rotational strength by the Rydberg transition, 46–51 kK, and a major negative rotational strength by the valence shell transition at higher frequencies (Fig. 8).

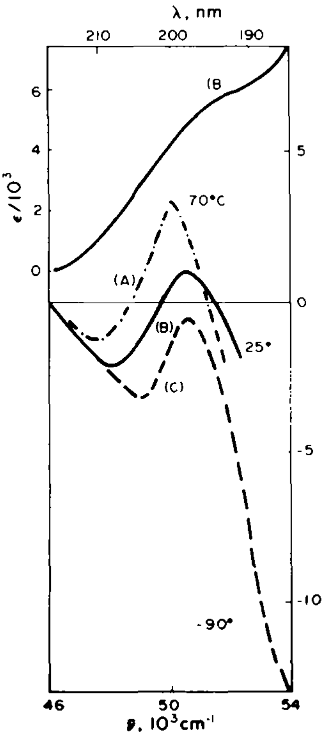

Fig. 7. The absorption spectrum (upper curve) and CD spectra (lower curves) of 4α-hydroxy-cholest-5-ene **6**, in *iso*-octane, (A) at +70°, (B) at +25° and (C) at −90°C.

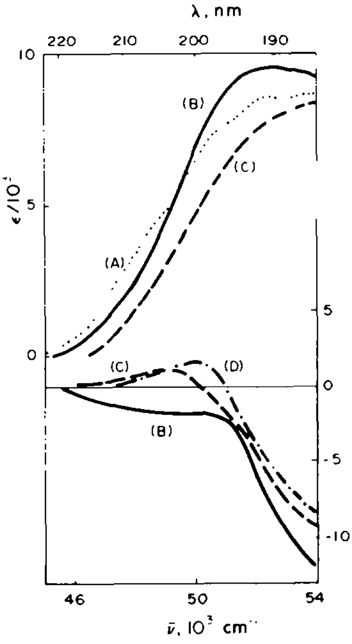

Fig. 8. The absorption spectra (upper curves) and CD spectra (lower curves) in *iso*-octane at 20°C of (A) Δ^5-cholestene **5**, (B) 4,4-dimethylcholest-5-ene **9**, (C) 4β-hydroxy-cholest-5-ene **7** and (D) 3β-hydroxy-cholest-5-ene **8**.

In general the effect of the substituents studied in the derivatives **6–9** upon the Rydberg CD band of Δ^5-cholestene **5** resembles that of an increase in the internal pressure of the solvent produced by cooling (Figs. 6–8). The room temperature CD spectrum of **6** is similar to that of the parent olefin **5** at low temperature (Figs. 6 and 7), and the two methyl substituents of **9** give rise to a perceptible blue-shift of the isotropic absorption in the Rydberg region 45–49 kK, in contrast to the small red-shift produced at the band maximum (190 nm) where the contribution of the valence-shell transition is dominant (Fig. 8). The principal result of the blue-shift at lower frequencies produced by the substituents of the derivatives **6–9** is that, at a given temperature in a paraffin solvent, the minor positive Rydberg rotational strength is more extensively overlapped than in the parent olefin **5** by the major negative valence-shell rotational strength at higher frequency, giving a smaller positive CD band or merely a shoulder or trough in the low-frequency wing of the major negative CD band (Figs. 6–8). In the CD spectra of the series **5–8** there is no evidence for the proposed[5] anti-octant behaviour of the hydroxy group in the +XYZ octant rule[3–5] (Fig. 1) relating the type and the position of a substituent to the sign of the lowest-energy Cotton effect of chiral alkenes.

The olefin CD couplet

The spectra of a number of chiral alkenes exhibit two major CD bands with opposed signs and comparable areas in addition to the low-frequency Rydberg CD band in the cases where the latter is observed[17,18] (Figs. 2, 5, 9 and 10).

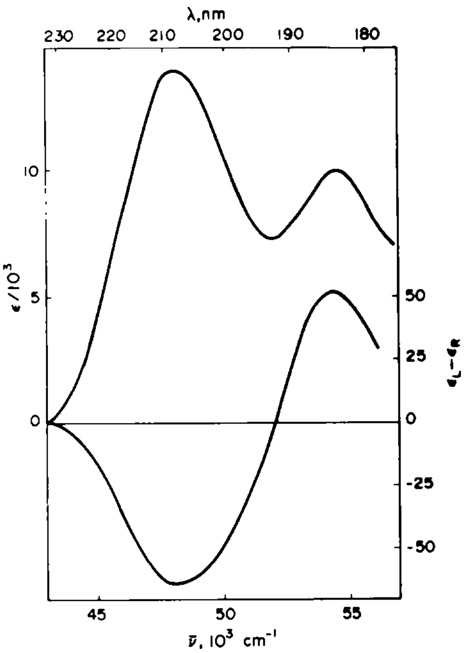

Fig. 9. The absorption (upper curve) and CD spectrum (lower curve) of (−)-fenchylidene fenchane **10** in *n*-pentane at 20°C.

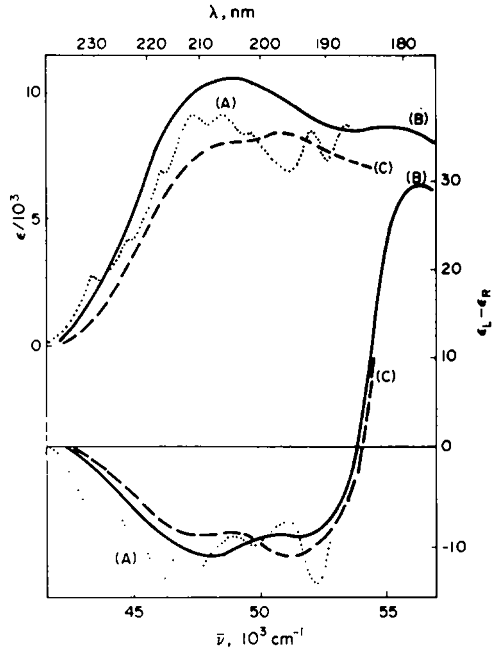

Fig. 10. The absorption spectra (upper curves) and CD spectra (lower curves) of (−)-cyclohexylidene bornane (**11**) (A) in the vapour phase and (B) in *n*-pentane solution and (C) of (−)-cyclohexylidene fenchane in *n*-pentane solution at 20°C.

Each major CD band of the couplet is associated with an isotropic absorption band which, for a given chiral olefin, have similar intensities (Figs. 2, 5, 9 and 10). The isotropic absorption bands at 48 and 55 kK of (−)-fenchylidene-fenchane[29] **10** (Fig. 9) and (−)-cyclohexylidenebornane **11** (Fig. 10), which are associated in each case with the lower and the higher energy CD band of the couplet, respectively, correspond to two bands at the same positions in the spectrum of the related achiral olefin, cyclohexylidene-cyclohexane **12**, which has been investigated by polarised single-crystal spectroscopy.[30] The study shows[30] that both the 48 and the 55 kK bands of **12** are stricly z-polarised along the direction of the C=C bond (Fig. 1) and that there is no appreciable perpendicularly-polarised absorption below 58 kK.

The 55 and the 48 kK band of **12** were ascribed,[30] respectively, to the $\pi_x \rightarrow \pi_x^*$ transition of the olefin chromophore and to a $\sigma_z \rightarrow \sigma_z^*$ transition, each having individually a z-polarised electric dipole moment. The assignment is improbable, however, as these particular transitions cannot give rise to the strong couplet of oppositely-signed CD bands near 48 and 55 kK, and the associated isotropic absorption, observed in the spectra of the analogous olefins **10**, **11**, (−)-cyclohexylidene-fenchane[29] (**13**) and (−)-*transoid*-2-bornylidene-bornane[31] **14**, or the less closely related pinenes **1** and **4** (Table 1, Figs. 2, 5, 9 and 10). An oppositely-signed CD couplet is generated by the interaction of two electric transition dipoles only if the two moments have a finite separation in the molecule and are non-coplanar, having orthogonal components.[32]

An oppositely-signed CD couplet originates from the interaction of two collinear transition moments in a randomly-oriented chiral molecule only if one is an electric and the other a magnetic dipole or, more generally, an electric and a magnetic multipole of the same order.[33] The polarised single-crystal spectrum[30] of **12** thus implies that the major CD couplet in the spectra of chiral olefins arises from the admixture by perturbation of an electric- and a magnetic-dipole zero-order excitation, each with z-polarisation. In the spectrum of ethylene the $\pi_x \rightarrow \pi_x^*$ transition, with a z-polarised electric dipole moment, is accompanied by a near-degenerate quadrupole transition[24] which, if of the form $\pi_x \rightarrow \pi_y^*$ or $\pi_y \rightarrow \pi_x^*$ (Fig. 1), has the xy-component of an electric quadrupole and the z-component of a magnetic dipole as the leading transition moments.

On energy grounds the zero-order excitation mixed with the $\pi_x \rightarrow \pi_x^*$ transition to the major degree in chiral alkenes is probably $\pi_x \rightarrow \pi_y^*$. The photoelectron spectra of **1**, **11** and **12**, and many other olefins,[23,34] show that the second ionisation potential, from π_y, lies 12–13 kK above the first, from π_x. Electron repulsion changes may reduce the energy-interval between the $\pi_x \rightarrow \pi_x^*$ and $\pi_y \rightarrow \pi_x^*$ excitations, but it is improbable that they render these zero-order transitions quasi-degenerate, as is observed for the $\pi_x \rightarrow \pi_x^*$ and the quadrupole transition of ethylene.[24] Accordingly the major CD couplet of chiral alkenes is taken to arise primarily from the mixing of the zero-order excitations, $\pi_x \rightarrow \pi_x^*$ and $\pi_x \rightarrow \pi_y^*$ (Fig. 1).

The observation that the isotropic absorption bands associated with the CD couplet of a given chiral alkene have comparable intensities (Table 1, Figs. 2, 5, 9 and 10) indicates that the $\pi_x \rightarrow \pi_x^*$ and $\pi_x \rightarrow \pi_y^*$ excitations are virtually degenerate in the substituted olefin, and that the corresponding excited configurations, $|xx^*\rangle$ and $|xy^*\rangle$, respectively, contribute with nearly equal weight to the upper stationary states of the two resultant transitions. The upper states of the 48 and the 55 kK transition of a chiral olefin, ψ_+ and ψ_-, respectively, may be expressed as the linear combinations,

$$\psi_+ = C_1|xx^*\rangle + C_2|xy^*\rangle \quad (1)$$

and

$$\psi_- = C_2|xx^*\rangle - C_1|xy^*\rangle \quad (2)$$

Table 1. The frequency, $\bar{\nu}(10^3\,\mathrm{cm}^{-1})$, and extinction coefficient, ϵ or $\Delta\epsilon = \epsilon_L - \epsilon_R$, of the band maxima in the absorption and CD spectra of chiral alkenes, together with the dipole strength, D$(10^{-36}$ c.g.s.), and rotational strength, R$(10^{-40}$ c.g.s.), obtained from the band areas of the oppositely-signed CD couplet and the associated isotropic absorption

	Absorption			Circular dichroism		
Olefin	$\bar{\nu}$	ϵ	D	$\bar{\nu}$	$\Delta\epsilon$	R
(−)-α-pinene **1**[a]	49.7	4900	4.7	49.6	−4.0	−6
	56.5	5200	5.1	54.4	+12.5	+16
(−)-β-pinene **4**[a]	50.1	10,800	7.9	49.9	+17.1	+35
	55.4	9000	~8	55.9	−17.0	−31
(−)-fenchylidene	48.1	14,000	13.4	48.1	−64.0	−160
fenchane **10**[b]	54.5	10,100	8.5	54.4	+51.0	+71
(−)-cyclohexylidene	48.7	10,600	14.0	48.0	−11.0	−48
bornane **11**[b]	55.0	8600		56.3	+29.0	+50
(−)-R-*trans*-	51.0	7600	7.0	51.0	−36.0	−92
cyclooctene **15**[c]	62.0	6900		63.9	+36.0	+88
(−)-transoid-2-	46.7	10,600		47.2	−28.0	
bornylidene bornane **14**[d]				53.8	+20.0	
cyclohexylidene	47.5	7500				
cyclohexane **12**[a]	54.9	8400				

[a] Vapour phase values.
[b] Values for n-pentane solution.
[c] Ref. 17.
[d] Ref. 11.

where the orbitals with occupation numbers unchanged by the excitations are omitted from the state functions and the configurational functions are contractions representing singlet determinantal forms, e.g.

$$|xx^*) = (1/\sqrt{2})[\pi_x(1)\pi_x^*(2) - \pi_x^*(1)\pi_x(2)]. \qquad (3)$$

The ground state function, ψ_0, is similarly abbreviated to $|xx)$, representing the doubly-occupied π-orbital, $[\pi_x(1)\pi_x(2)]$, from which each of the zero-order excitations originate. The ratio of the dipole strength of the 48 to that of the 55 kK olefin absorption band, measured by the observed frequency-weighted band area, gives the relative magnitude of the configurational mixing coefficients through the relation,

$$D_{0+}/D_{0-} = (C_1/C_2)^2 \qquad (4)$$

since the magnetic dipole and electric quadrupole strength of $\pi_x \rightarrow \pi_y^*$ is negligible compared with the electric dipole strength of $\pi_x \rightarrow \pi_x^*$. The ratio $|C_1/C_2|$ obtained from relation (4) is found to lie in the range from 0.96 for **1** to 1.26 for **10**, so that generally $|C_1| \sim |C_2|$ and the electric-dipole and the magnetic-dipole excited configuration contribute nearly equally to each of the excited states (1) and (2).

The energy of a transition from the ground state, ψ_0, to the olefin excited states, ψ_+ and ψ_-, E_{0-} and E_{0-}, respectively, is related to the zero-order configurational excitation energies, E_{xx^*} and E_{xy^*}, by the expression,

$$E_{0\pm} = (1/2)(E_{xx^*} + E_{xy^*}) \pm (xx^*|V|xy^*)/(2C_1C_2) \qquad (5)$$

where $(xx^*|V|xy^*)$ is the matrix element of the Coulombic potential between the charge distributions of the configurational excitations. The observable energy-separation, $(E_{0-} - E_{0+})$ may be expressed in terms of this matrix element or, equivalently, through the orthogonality condition between the excited states (1) and (2), by the relation,

$$\Delta E = (E_{0-} - E_{0-}) = (E_{xx^*} - E_{xy^*})/C_2^2 - C_1^2). \qquad (6)$$

The observed frequency interval between the olefin bands near 48 and 55 kK and the coefficients, C_1 and C_2, obtained from eqn (4) and the normalisation condition, give the separation $(E_{xx^*} - E_{xy^*})$ between the zero-order excited configurations values in the range from +300 cm^{-1} for **1** to −1500 cm^{-1} for **10**. These values are comparable to the interval of +1200 cm^{-1} between the $\pi_x \rightarrow \pi_x^*$ and the quadrupole transition of ethylene.

The small zero-order energy separation $(E_{xx^*} - E_{xy^*})$ implies that the near-degenerate excitations $\pi_x \rightarrow \pi_x^*$ and $\pi_x \rightarrow \pi_y^*$ of the planar D_{2h} olefin chromophore are extensively mixed by minor perturbations removing the symmetry distinction between the $|xx^*)$ (B_{1u}) and the (B_{1g}) $|xy^*)$ excited configurations. Oscillatory perturbations which are non-totally-symmetric, notably the pseudoscalar (a_u) torsional vibrational mode (ν_4) of the chromophore partition the dipole strength of the $\pi_x \rightarrow \pi_x^*$ excitation between the two resultant states terminating in the mixed excited states (1) and (2). At the turning-points of the ν_4 torsional mode the olefin chromophore has a D_2 nuclear symmetry where both of the excited configurations $|xx^*)$ and $|xy^*)$ transforms as B_1 and are mixed. The achiral olefin **12** is expected to have a ν_4 torsion mode frequency of some 300 cm^{-1} in the electronic ground state with a 30% population of vibrationally excited molecules at ambient temperature. At −183°C in 3-methylpentane solution the 48 and 55 kK room temperature bands of the olefin **12** merge under a common envelope, conserving the total band area, with a maximum near 50 kK. The reduction in the frequency interval between the two bands probably arises from the restriction of molecules of **12** to the zero level of the ν_4 and other non-totally symmetric vibrational modes at liquid nitrogen temperatutes, the perturbations arising from the zero-point amplitudes of these modes being small.

While the torsional-mode mechanism may account for the two z-polarised isotropic absorption bands given by **12** and other achiral olefins[23] near 48 and 55 kK, it provides no explanation for the oppositely-signed CD couplet exhibited by chiral alkenes in the same frequency region. The ν_4 torsion mode with mirror-image turning points takes the olefin chromophore from the R-configuration in D_2 symmetry to an enantiomeric S-configuration so that no electronic transition of the chromophore is optically-active on a time-average. A chiral-deformation mechanism for optical activity in the olefin chromophore requires a non-zero torsion angle at the equilibrium nuclear configuration or, less restrictively, inequivalent turning-points in each level of the ν_4 torsional mode, giving a non-vanishing torsion angle on a time-average (Fig. 11). For a π-bond torsion angle in the range, $0 < \theta < \pi/2$, the $\pi_x \rightarrow \pi_x^*$ excitation develops an electric quadrupole moment in the xy-plane proportional to sin θ, the xy-electric quadrupole moment of the $\pi_x \rightarrow \pi_y^*$ excitation being proportional to cos θ. The Coulombic potential between the two quadrupolar transition moments, representing the matrix element $(xx^*|V|xy^*)$ (eqn 5), is negative for the lower-energy resultant transition, $\psi_0 \rightarrow \psi_+$. This condition imposes a phase relationship upon the constituent configurational transition moments (eqn 1), such that the electric dipole moment μ_{xx^*} of the $\pi_x \rightarrow \pi_x^*$ excitation is parallel to the magnetic dipole moment m_{yx}^* of the $\pi_x \rightarrow \pi_y^*$ excitation for a negative angle of π-bond torsion (Fig. 11), giving a positive rotational strength, R_{0+}, for the lower-frequency member of the olefin CD couplet.

A torsion of the π-bond in an alkene produces an inherently dissymmetric olefin chromophore and each dipole-allowed excitation develops an intrinsic rotational strength. In particular the $\pi_x \rightarrow \pi_x^*$ excitation acquires a magnetic moment, m_{xx^*}, and the $\pi_x \rightarrow \pi_y^*$ excitation an electric moment, μ_{xy^*}, each of these moments[14] being proportional to sin θ. However, the torsion-induced moments are quite minor[14] for small and physically-realisable angles of twist relative to the allowed moment of each of the two excitations in the coplanar olefin chromophore. Thus the rotational strengths of the transitions giving the olefin CD couplet in the far UV region may be approximated on a simple two-configuration basis by,

$$R_{0+} = -R_{0-} = -i(\mu_{xx^*} \cdot m_{y^*x})C_1C_2 \qquad (7)$$

where μ_{xx^*} and m_{y^*x} are the zero-order dipole moments of the configurational excitations, respectively, electric for $\pi_x \rightarrow \pi_{x^*}$ and magnetic for $\pi_x \rightarrow \pi_{y^*}$. The product C_1C_2 of the weighting coefficients (eqns 1 and 2) is (1/2) for exact

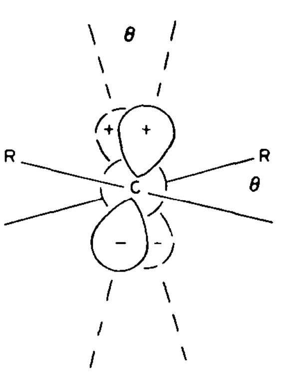

Fig. 11. A negative π-bond torsion angle θ giving the lower- and the higher-frequency member of the olefin CD couplet a positive and a negative rotational strength, respectively.

configurational degeneracy, but more generally the product is given by the ratio,

$$C_1C_2 = -(xx^*|V|xy^*)/\Delta E \qquad (8)$$

from eqns (5) and (6). The higher-frequency rotational strength R_{0-} is of opposite sign to R_{0+} as the Coulombic potential between the two configurational quadrupole transition moments is necessarily repulsive (postive) for the higher energy transition, $\psi_0 \rightarrow \psi_-$, requiring the configurational dipole transition moments, μ_{xx^*} and m_{y^*x}, to be antiparallel for a positive torsion angle (Fig. 11).

Models indicate that the steric hindrance to the coplanarity of the atoms of the olefin chromophore is severe in the exocyclic tetrasubstituted alkenes studied, the strain decreasing in the order **10** > **14** > **13** > **11**. The π-bond torsion angle is positive (Fig. 11) for these alkenes and in each case the negative and the positive band of the CD couplet are found to lie at the lower and the higher frequency, respectively (Table 1, Figs. 9 and 10). The correspondingly-signed CD bands of (−)-R-*trans*-cyclooctene[35] **15** lie in the same frequency-order,[17] and in **15** the π-bond torsion angle is also positive[36] lying in the range from[37] +23° to[36] +42°. The experimental[17] dipole and rotational strength of the 51 kK absorption and CD band of **15** give the transition $\psi_0 \rightarrow \psi_+$ an electric moment of 2.6 Debye and a magnetic moment of 0.35 Bohr magneton on the assumption that these moments are wholly collinear and antiparallel. The same assumption and the corresponding data for **10** (Table 1) indicate that the 48.1 kK transition of this olefin has an electric and a magnetic moment of 3.6 Debye and 0.44 Bohr magneton, respectively. These values for the transition moments are consistent with a π-bond torsion model for the olefin CD couplet, whereby the $\pi_x \rightarrow \pi_x^*$ excitation, with an electric moment of 3.4 Debye in the case of ethylene, and the $\pi_x \rightarrow \pi_y^*$ excitation, with an expected magnetic moment in the region of one Bohr magneton, are mixed by the torsion of the chromophore, and the configurational moments are partitioned between the resultant transitions, $\psi_0 \rightarrow \psi_\pm$ (eqns 1 and 2).

The low-frequency Rydberg transition $\pi_x \rightarrow 3s$ develops an intrinsic rotational strength when the olefin chromophore through torsion becomes inherently dissymmetric. For a negative π-bond torsion angle (Fig. 11) the $\pi_x \rightarrow 3s$ transition acquires an x-polarised magnetic moment parallel to the zero-order electric moment. The resulting positive rotational strength has the same sign as the lower-frequency member, R_{0+}, of the olefin CD couplet (eqn 7). Having the same sign as the adjacent and stronger CD band, due to the $\psi_0 \rightarrow \psi_-$ transition, the Rydberg CD band is not readily detected in the spectra of chiral alkenes owing their optical activity primarily to π-bond torsion. The Rydberg $\pi_x \rightarrow 3s$ CD absorption has been observed in the vapour-phase spectrum of **15** and it is found to have the same sign as the adjacent major CD band at higher frequency.[17] There is little evidence of a $\pi_x \rightarrow 3s$ Rydberg CD absorption in the solution spectra of the hindered olefins **10**, **11** or **13**, but a discontinuity in the vibronic structure of the vapour-phase spectrum of **11** near 48 kK (Fig. 10) suggests that the Rydberg and valence-shell rotational strength are both negative and overlie one another. Similarly the Rydberg CD absorption of (+)-twistene **16**, if present, must be positive and overlaid by the strong positive rotational strength R_{0+} at 50 kK (Fig. 12) connected with the marked negative π-bond torsion angle θ of the olefin chromophore (Fig. 11)

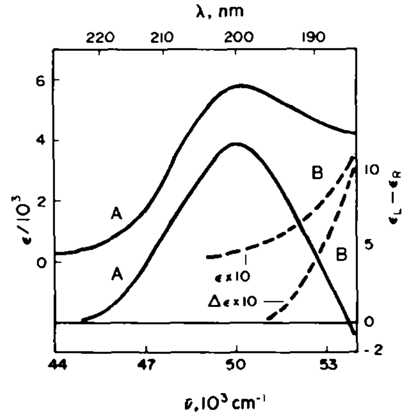

Fig. 12. The absorption (upper curves) and CD spectra (lower curves) of, (A) (+)-twistene **16** and (B) (+)-twistane in *iso*-octane at 20°.

indicated by a model of the absolute configuration[38] **16** of (+)-twistene.

The Rydberg CD band of (−)-α-pinene **1** has a sign opposed to that of the adjacent CD band due to the $\psi_0 \rightarrow \psi_-$ transition, like (+)-camphene **2** and (−)-bornene **3** (Figs. 2–4), and it is probable from the structural evidence[39–41] that neither these terpenes nor (−)-β-pinene **4** owe their optical activity primarily to π-bond torsion. Electron diffraction studies indicate that the C=C bond of α-pinene **1** and the three carbon atoms to which it is attached share a common plane,[39] and neither X-ray[40] nor electron diffraction[41] methods reveal any significant distortion of the olefin chromohore in β-pinene **4**. These observations suggest that the couplet of oppositely-signed CD bands given by (−)-α- and (−)-β-pinene in the far UV region (Figs. 2 and 5) arise from the mixing of the excited configurations |xx*) and |xy*) under either a static[42] or a dynamic[43] perturbation of the symmetric olefin chromophore by dissymmetrically-located substituents.

Static field mechanism

A static perturbation of the zero-order electronic states of the olefin chromophore is afforded by the Coulombic potential due to the ground-state charge distribution of the substituents. If the potential has a pseudoscalar component, transforming under the A_u representation of D_{2h}, the electric-dipole $\pi_x \rightarrow \pi_x^*$ and magnetic-dipole $\pi_x \rightarrow \pi_y^*$ excitation are mixed to give each resultant transition a non-vanishing rotational strength[42] (eqn 7). The perturbational matrix element (xx*|V|xy*) connecting the two zero-order chromophore excitations (eqn 8) is now represented by the Coulombic potential between the transitional charge distribution of the virtual excitation $\pi_x^* \rightarrow \pi_y^*$ of the chromophore and the stationary charge distribution of the substituent L in its ground electronic state L_0,

$$(xx^*|V|xy^*) = (x^*y^*|V|L_0L_0). \tag{9}$$

The leading moment of the transitional charge distribution |x*y*) is the xyz-component of an electric octupole (Fig. 13) which has A_u symmetry in D_{2h}. The effective component of the potential arising from the stationary charge distribution of the substituent $|L_0L_0)$ has the same symmetry and, at its simplest, the same functional form if the matrix element (eqn 9) is non-zero.[42]

The electric and the magnetic dipole moment of the excitations $\pi_x \rightarrow \pi_x^*$ and $\pi_x \rightarrow \pi_y^*$, respectively, are parallel, giving a positive rotational strength, when the electric octupole moment of the virtual transition $\pi_x^* \rightarrow \pi_y^*$ has the form depicted (Fig. 13). These dipole transition moments are antiparallel, producing a negative rotational strength, if the positive and negative signs of the octupole moment, representing an excess and a deficit of electronic charge density, respectively, are interchanged. If a group bearing a positive charge is substituted into an octant region, defined by the X, Y and Z axes of the chromophore, where the octupole moment sign is positive (a local excess of electronic charge) the Coulombic energy is lowered

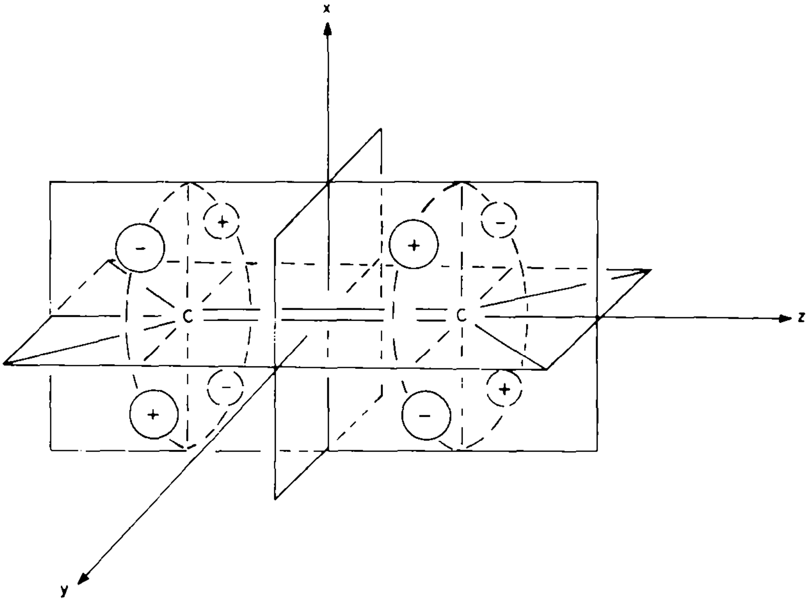

Fig. 13. The electric octupole moment of the $\pi_x^* \rightarrow \pi_y^*$ transition corresponding to parallel electric and magnetic dipole moments for the $\pi_x \rightarrow \pi_x^*$ and $\pi_x \rightarrow \pi_y^*$ transition, respectively. A substituent bearing an effective positive charge located in an octant for which the coordinate-product XYZ is positive lowers the Coulombic potential and affords the lower-frequency member of the olefin CD couplet a positive rotational strength.

(Fig. 13). The rotational strength is then positive for the lower-energy member, R_{0+}, of the olefin CD couplet in the far UV region. In contrast, if a positively charged group is substituted into an octant spatial region where the octupole moment sign is negative (a local positive hole in the electronic charge distribution) the energy is raised, and the rotational strength is then positive for the higher-energy member, R_{0-}, of the olefin CD couplet. Thus, the sign of the lower-energy band of the olefin CD couplet follows that of the product function +XYZ of the coordinates of the substituent in the chromophore frame, whereas the sign of the higher-energy CD band of the couplet follows that of the product function −XYZ (Figs. 1 and 13).

These static-field octant rules for chiral alkenes rest on the assumptions that the olefin CD couplet arises from the transitions $\psi_0 \rightarrow \psi_\pm$ (eqns 1 and 2), and that the common organic substituents bear an effective positive charge. The empirical octant rule for chiral olefins,[3] +XYZ (Fig. 1), refers to the lowest-frequency CD band in the spectrum with the additional rule[4,5] −XYZ for the adjacent CD band to higher energies. These CD bands are not necessarily due to the transitions $\psi_0 \rightarrow \psi_\pm$ nor to the unmixed constituent excitations,[4,5] $\pi_x \rightarrow \pi_x^*$ and $\pi_x \rightarrow \pi_y^*$, owing to the appearance of the lowest-energy Rydberg transition, as the cases **1**–**3** and **5**–**9** illustrate (Figs. 2–4, 6–8).

From the static-field viewpoint the particular signs of the olefin octant rules for the transitions $\psi_0 \rightarrow \psi_\pm$ are interchanged if the substituent group is negatively charged. Most of the organic anionic groups absorb in the frequency region of the olefin CD couplet, limiting studies of the expected sign-reversal with such substituents in a chiral alkene. However, ammonium ions are still transparent at 55 kK and a study of the effect of positively-charged substituents is feasible. The CD spectrum of the dication of conessine **17** shows that the effect of the 3β-dimethylammonium group upon the optical activity of Δ^5-cholestene is small, being comparable to that of the neutral 3β-hydroxy group in cholesterol **8** (Fig. 14). The CD spectrum of the neutral molecule of conessine **17** indicates that the 3β-dimethylamino group has the more profound effect (Fig. 14), probably on account of the transitions involving the lone-pair electrons of the amino-group, $n \rightarrow \sigma^*$, near 45 and 52 kK.

Dynamic coupling mechanism

While the static field approach[42] is concerned primarily with the substituent-induced mixing of chromophore transitions, the first-order dynamic coupling method[43,44] deals only with a single transition of the chromophore, electric or magnetic-dipole allowed, and its Coulombic coupling to a transient induced electric dipole in a dissymmetrically-located substituent. A first-order dynamic coupling treatment of the electric-dipole $\pi_x \rightarrow \pi_x^*$ transition of chiral alkenes has been reported[45] based on the assumption that the lowest-energy CD band is due to this transition. It is found that the most satisfactory account of the observed rotational strength of this CD band requires the assignment of a negative polarisability anisotropy $(\alpha_\parallel - \alpha_\perp)$ to the single C–C bond.[45] Of the fifteen different sets of the components of the polarisability tensor for the single C–C bond listed by Le Fèvre *et al.*[46] only the earliest, due to Sachsse,[47] is negative. The polarisability anisotropy of a given bond cannot be determined unequivocally, except for diatomic molecules, as the components of the polarisability tensor are non-additive over the bonds of a molecule, although the mean polarisability is strictly bond- or group-additive.[48,49] While the proposed values of $(\alpha_\parallel - \alpha_\perp)$ for the C–C bond cover a wide range, this quantity is generally taken to be positive.[46,50]

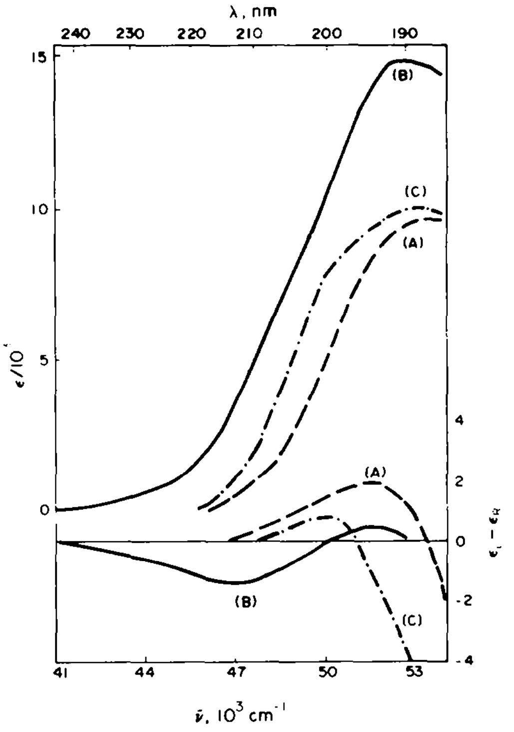

Fig. 14. The absorption spectra (upper curves) and CD spectra (lower curves) of (A) the dication of conessine **17** in 2,2,2-trifluoroethanol, (B) the neutral molecule of conessine in *iso*-octane/ethanol 4/1, and (C) of cholesterol **8** in *iso*-octane at 20°.

The application of the first-order dynamic coupling method to the olefin $\pi_x \rightarrow \pi_x^*$ transition leads to no general sector rule as the sign and magnitude of the rotational strength becomes a function not only of the position of the substituent but also of the orientation of the principal bond or group axis of the substituent in the chromophore frame.[43] The analogous treatment of the magnetic-dipole $\pi_x \rightarrow \pi_y^*$ transition of chiral alkenes, taking into account only the mean polarisability $\bar{\alpha}$ of a substituent, affords the sector rule +XYZ for the sign of the corresponding rotational strength as a function of the position of the substituent group (Fig. 1). Overall the expectations of the first-order dynamic coupling model are the overlap of the unrelated rotational strengths of the transitions $\pi_x \rightarrow \pi_x^*$ and $\pi_x \rightarrow \pi_y^*$ in a common frequency region, giving two CD bands which do not in general have the opposed signs and comparable magnitudes characteristic of the olefin CD couplet.

On carrying the treatment of the symmetric chromophore in a dissymmetric molecular environment to the second order a mechanism emerges whereby an electric and a magnetic dipole allowed transition of the chromophore are mixed by the Coulombic coupling of the leading electric multipole moment of each of these transitions with the transient electric dipole induced in the substituent.[51] The mechanism is particularly significant in cases, such as that of the olefin CD couplet, where the chromophore electric and magnetic dipole transition are degenerate, or nearly so. It is envisaged in the application of the mechanism to chiral alkenes that the electric dipole moment of the $\pi_x \rightarrow \pi^*_x$ transition correlates Coulombically an electric dipole induced in the substituent, proportional to the mean polarisability of the latter, $\bar{\alpha}(L)$, and that the substituent dipole in turn Coulombically correlates the electric quadrupole moment of the $\pi_x \rightarrow \pi^*_y$ transition (Fig. 15). Thereby the olefin excitations $\pi_x \rightarrow \pi^*_x$ and $\pi_x \rightarrow \pi^*_y$ are mixed and a particular phase relationship is introduced between the respective electric dipole and magnetic dipole transition moment.

In effect the matrix element $(xx^*|V|xy^*)$ (eqn 8) connecting the olefin excited configurations $|xx^*)$ and $|xy^*)$ is separated into two further elements. One expresses the Coulombic potentitial between $|xx^*)$ and the charge distribution of the substituent transition $L_0 \rightarrow L_l$ and the other represents the corresponding potential between $|L_0L_l)$ and $|xy^*)$,

$$(xx^*|V|xy^*) = \sum_{l \neq 0} (xx^*|V|L_0L_l)(L_0L_l|V|xy^*)/(E_{0l} - E_{xx^*}) \qquad (10)$$

where E_{0l} is the energy of the substituent transition $L_0 \rightarrow L_l$. Each of the transitional charge distributions in eqn (10) is expanded in a multipole series around an appropriate centre, the chromophore origin in the case of $|xx^*)$ and $|xy^*)$ and the substituent origin for $|L_0L_l)$. Each series is truncated after the leading term. The term retained for $|xx^*)$ is the z-polarised electric dipole transition moment, $\mu^z_{xx^*}$, while that for $|xy^*)$ is the xy-component of the electric quadrupole moment, $\theta^{xy}_{xy^*}$. The expansion of $|L_0L_l)$ affords the electric dipole moment $\vec{\mu}_{0l}$ which, in general, has three Cartesian components.

Each of the matrix elements on the right-hand side of eqn (10) is now expressed in terms of the Coulombic potential between two point dipoles, or a point dipole and a point quadrupole, as a function of the coordinates (X, Y, Z) of the substituent in the chromophore frame,[43]

$$(xx^*|V|L_0L_l) = -\mu^z_{xx^*}\cdot[3XZ\mu^x_{0l} + 3YZ\mu^y_{0l} + (3Z^2 - R^2)\mu^z_{0l}]R^{-5} \qquad (11)$$

and

$$(L_0L_l|V|xy^*) = 3\theta^{xy}_{xy^*}\cdot[Y(R^2 - 5X^2)\mu^x_{0l} + X(R^2 - 5Y^2)\mu^y_{0l} - 5XYZ\mu^z_{0l}]R^{-7} \qquad (12)$$

where R is the distance between the substituent and the chromophore origin. The substitution of eqns (11) and (12) into eqn (10), followed by a summation over the excited states L_l of the substituent on the assumption that the latter is isotropic, gives the approximate relation,

$$(xx^*|V|xy^*) = 12\mu^z_{xx^*}\cdot\theta^{xy}_{xy^*}\cdot\bar{\alpha}(L)[XYZ]R^{-10} \qquad (13)$$

where $\bar{\alpha}(L)$ is the isotropic or average polarisability of the substituent at the mean frequency of the near-degenerate zero-order excitations, $\pi_x \rightarrow \pi^*_x$ and $\pi_x \rightarrow \pi^*_y$. Substitution of eqn (13) into eqns (7) and (8) gives the rotational strength of the lower-, R_{0+}, and the higher-frequency, R_{0-}, members of the olefin CD couplet through the relation,

$$R_{0-} = -R_0 = -12i m^z_{y^*x}\theta^{xy}_{xy^*}|\mu^z_{xx^*}|^2\bar{\alpha}(L)[XYZ]R^{-10}(\Delta E)^{-1}. \qquad (14)$$

In eqns (13) and (14) an energy-ratio of the order of unity is omitted.

The lower-energy Coulombic correlation between the chromophore electric dipole moment $\mu^z_{xx^*}$ and the transient induced electric dipole in the substituent, and between the latter dipole and the electric quadrupole moment of the chromophore $\theta^{xy}_{xy^*}$, give the phase relation illustrated (Fig. 15) between the excitations $\pi_x \rightarrow \pi_{x^*}$ and $\pi_x \rightarrow \pi_{y^*}$. The respective electric $\mu^z_{xx^*}$ and magnetic dipole $m^z_{y^*x}$ moment of those excitations are parallel, giving a positive rotational strength for the lower-energy member of the olefin CD couplet R_{0+}, if the substituent is located in an octant for which the coordinate product (XYZ) (eqn 14) is positive (Fig. 15). The sector rule for R_{0+} is thus +XYZ and that for the higher-frequency member of the CD couplet R_{0-} is −XYZ.

The second-order dynamic coupling mechanism affords

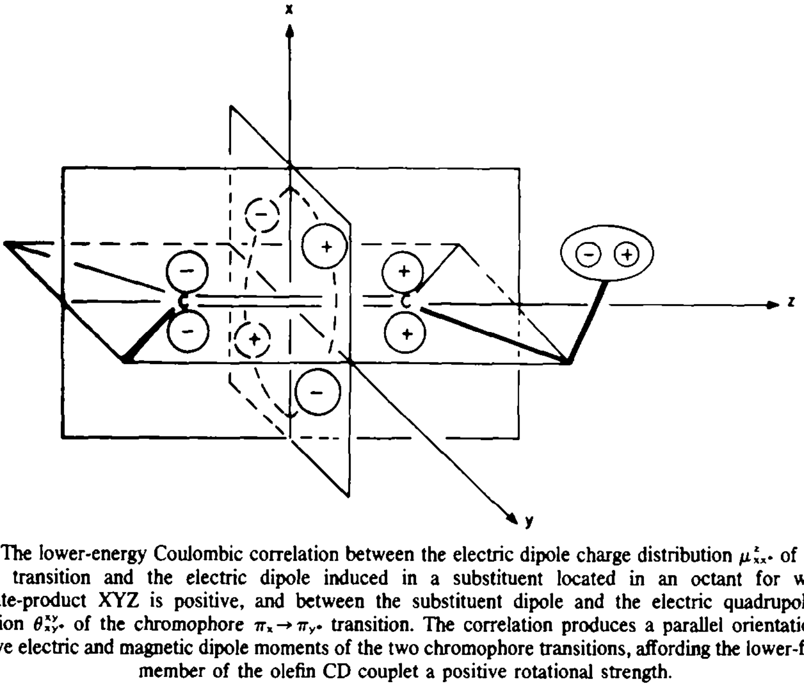

Fig. 15. The lower-energy Coulombic correlation between the electric dipole charge distribution $\mu^z_{xx^*}$ of the olefin $\pi_x \rightarrow \pi_{x^*}$ transition and the electric dipole induced in a substituent located in an octant for which the coordinate-product XYZ is positive, and between the substituent dipole and the electric quadrupole charge distribution $\theta^{xy}_{xy^*}$ of the chromophore $\pi_x \rightarrow \pi_{y^*}$ transition. The correlation produces a parallel orientation of the respective electric and magnetic dipole moments of the two chromophore transitions, affording the lower-frequency member of the olefin CD couplet a positive rotational strength.

the same qualitative sector rules for chiral alkenes as the first-order static field model based upon the assumption that the substituent carries an effective positive charge. No sign-reversal of the olefin octant rules for a negatively-charged substituent is expected by the dynamic coupling mechanism, however. The two mechanisms differ moreover in the expected dependence of the rotational strengths R_{0+} and R_{0-} of the CD couplet upon the distance R between the substituent and the chromophore origin. For the dynamic-coupling mechanism the dependency is R^{-7} (eqn 14), whereas it is R^{-4} for the point-octupole-charge potential of the static-field model (eqn 9). Both of these distance-dependencies, particularly the former, are unrealistically short-range for substituents close to the olefin chromophore, such as an allylic group, since they are based upon the point-multipole approximation for the transition moment potentials, e.g. eqns (11) and (12). The radial charge-density maximum of the quadrupole transition moment θ^{xy}_{xy}, is expected to lie at some 0.8 Å from the chromophore origin, and this distance is not negligible compared to the separation of 2.8 Å between the carbon atom of an axial allylic methyl group and that origin. In general an explicit consideration of the finite extension of the relevant transition multipole moment is required for a quantitative estimate of rotational strengths by either the static-field or dynamic-coupling method.[51] Each molecule or class of molecules then becomes a particular case, whereas the point-multipole approximation affords general, if only semi-quantitative, sector rules.

DISCUSSION

The sector rules +XYZ and −XZY for the lower- and the higher-frequency CD band arising from the mixed $\pi_x \rightarrow \pi^*_x$ and $\pi_x \rightarrow \pi^*_y$ excitations (eqns 1 and 2) of chiral alkenes appear to hold for a wide range of dissymmetric olefins,[3–5,11–13] but a number of exceptions have been noted, particularly amongst exocyclic methylene and alkylidene derivatives.[6–10] In studies of the CD spectra of chiral alkenes the corresponding isotropic absorption spectra are not always reported, so that a Rydberg CD band, found at low frequencies where the isotropic absotption is small, may be ascribed to a valence-state transition and interpreted by the sector rule to which that transition refers. In the absence of vapour-phase or variable-temperature CD studies to characterise the Rydberg CD band, a comparison of the absorption with the corresponding CD spectrum affords a guide to the nature of the transitions involved. Each CD band of the olefin valence-state couplet generally lies at a frequency where the associated isotropic absorption intensity is high, close to a maximum, whereas the Rydberg CD band usually lies at the low-energy band edge, far from the absorption maximum (Table 1, Figs. 2–10).

Transitions additional to the manifold discussed contribute to the CD absorption of chiral alkenes in the 250–165 nm region studied and these contributions limit the scope of the sector rules for the valence state CD couplet. The higher-energy CD band of the couplet in (+)-twistene **16** below 185 nm is probably overlaid by CD absorption of a $\sigma \rightarrow \sigma^*$ origin since the isotropic and CD absorption of (+)-twistane, although small, is detectable in the quartz UV region (Fig. 12). Similarly the corresponding CD band of Δ^5-cholestene **5** lies at a frequency higher than 59 kK if, as the temperature-variation suggests, the lowest-energy CD absorption has a Rydberg origin (Fig. 6). At 59 kK the isotropic and CD absorption of 5α-cholestane is already large (Fig. 16), suggesting that even the lower-energy member of the olefin CD couplet is partly overlaid by $\sigma \rightarrow \sigma^*$ absorption in Δ^5-cholestene **5**.

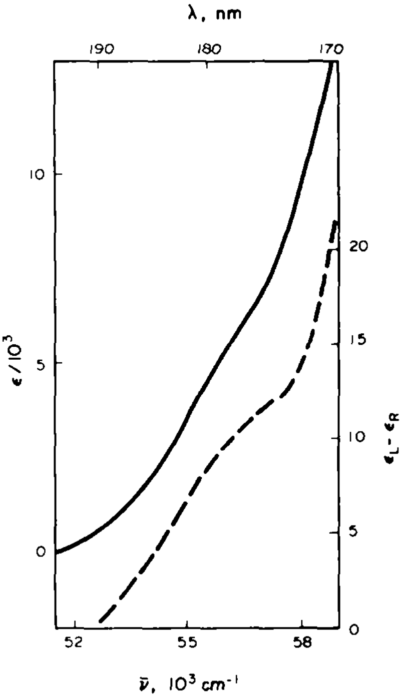

Fig. 16. The absorption (upper curve) and CD spectrum (lower curve) of 5α-cholestane in n-pentane at 20°C.

Although earlier excluded on energy grounds as the primary magnetic dipole transition giving rise to the olefin CD couplet, the $\pi_y \rightarrow \pi^*_x$ excitation is expected[14,15] to contribute to the rotational strengths of a chiral alkene. If particular substituents, or ring strain, produce a near degeneracy of the excitations $\pi_x \rightarrow \pi^*_x$ and $\pi_y \rightarrow \pi^*_x$, as opposed to the quasi-degeneracy of the former and $\pi_x \rightarrow \pi^*_y$ previously considered, the mixing mechanisms proposed would again account for the appearance of a couplet of oppositely-signed CD bands with comparable areas in the spectrum of a chiral alkene. However the sector rules would be the converse of those implied by the mixing of the $\pi_x \rightarrow \pi^*_x$ and $\pi_x \rightarrow {}^*_y$ excitations. By the torsion mechanism, the lower-energy member of the olefin CD couplet would be expected to have a negative rotational strength for a negative angle of π-bond torsion (Fig. 11). Both the first-order static field and the second-order dynamic coupling model would afford a −XYZ octant rule for the lower-frequency member, R_{0+}, of the couplet. The balance of the evidence at present, however, appears to support the +XYZ sector rule for this member implied by $\pi_x \rightarrow \pi^*_x$ and $\pi_x \rightarrow \pi^*_y$ mixing (Figs. 13 and 15).

EXPERIMENTAL

Materials

We thank colleagues for samples of the following chiral alkenes: Prof. D. H. R. Barton[29] (Imperial College, London) for (−)-fenchylidene fenchane **10** and (−)-cyclohexylidene fenchane **13**; Prof. M. Tichý[38] (Czechoslovak Academy of Sciences, Prague) for (+)-twistene **16** and (+)-twistane; and Dr. J. M. Coxon (University of Canterbury, New Zeland) for 4α-hydroxy-**6** and 4β-hydroxy-cholest-5-ene **7**.

The method of Barton *et al.*[29] afforded (−)-cyclohexylidene bornane **11** from (+)-camphor and cyclohexanone *p*-tolylsulphonyl hydrazone. The identity of **11** was established by ^1H and ^{13}C NMR and by mass spectrometry after purification by GLC. (−)-Bornene **3** was obtained by the method of Clement *et al.*,[52] Δ^5-cholestene **5** by Mauthner's method,[53] and 4,4-dimethylcholest-5-ene **11** according to Halsall *et al.*[54]

The alkenes **1**, **2**, **4**, **8**, **16** and were commercial samples recrystallised or purified by GLC. For the neat liquids $[\alpha]_D^{24}$ values were (−)-α-pinene **1**, −44.3°; (+)-camphene **2**, +71.0°; and (−)-β-pinene **4**, −21,0°; the CD spectra of **1** and **4** were corrected to optical purity, $[\alpha]_D^{24}$ −51.2° and −22.7°, respectively.

Spectrometer

A 1-metre concave-grating vacuum UV monochromator, previously described,[55] was modified for CD spectroscopy following earlier designs.[19–21] A magnesium fluoride Rochon prism was placed before the exit slit so that the latter separated the ordinary from the extraordinary beam. After the exit slit the radiation passes through a Morvue calcium fluoride acousto-optic modulator with the incident polarisation vector at π/4 to the principal directions of the modulator, and then the sample compartment to an EMI 6256S photomultiplier. The vacuum tank of the monochromator is sealed with a calcium fluoride plate from interchangeable sample compartments which, for solution studies, are constructed of minimum size and are flushed with oxygen-free nitrogen to facilitate change of sample. Cells are constructed of optically-flat calcium fluoride plates separated by foil or Teflon spacers 10–50μm thick. For absorption studies optical density measurements of both the solution and the corresponding solvent are made relative to nitrogen in order to monitor solvent transmission. Optimum transmission and solubility characteristics for the alkenes studied is afforded by *n*-pentane.[56]

Absorption and CD measurements down to 185 nm were carried out additionally with a Cary 17 and with a Jouan CD 185 and Jasco J40 C, respectively.

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