# Infrared Vibrational Circular Dichroism

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Summary Vibrational c.d. has been detected in the i.r. absorption spectrum of a cholesteric mesophase.

OPTICAL rotation in the i.r. wavelength region has been studied since 1836,[1] but vibrational Cotton effects have long eluded detection.[2] The experimental accessibility of c.d. depends upon the magnitude of the dissymmetry factor,[3] $g = [(\epsilon_l - \epsilon_r)/\epsilon]$, and the g-factor for a vibrational absorption is expected to be smaller than that of an electronic band in the ratio of the corresponding transition
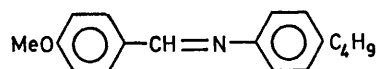
(I)

frequencies.[4] The g-factor is optimum in a helical array of skewed planar chromophores (Figure 1) when the helix pitch length, P, is of the order of the wavelength of light, λ. This condition may be realised in a cholesteric mesophase, and recently anomalous rotatory dispersion has been found[5] in the i.r. vibrational spectrum of N-(p-methoxybenzyl-idene)butylaniline (I), and related room-temperature nematic liquid crystals, perturbed into the cholesteric mesophase by the addition of a chiral solute.
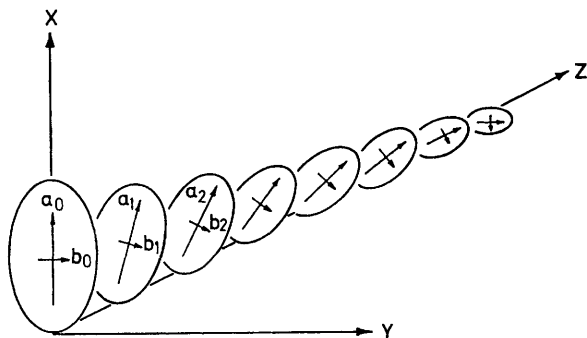

FIGURE 1. *Helical system of anisotropic planar chromophores.*

We report the i.r. c.d. detected in the vibrational absorption spectrum of (I) containing 2% of (−)-menthol (Figure 2). The measurements were made with an i.r. spectrophotometer adapted with wire-grid polarisers and Fresnel rhombs of sodium chloride to present to the sample studied left- and right-circular radiation in square-wave modulation at 10 Hz, followed by the monochromator and a thermocouple detector.

The theory of the optical properties of the cholesteric mesophase,[6—9] recently extended to wavelength regions of absorption,[10] indicates two main sources for the vibrational c.d. observed (Figure 2). A cholesteric mesophase consisting of skewed birefringent layers, each with the refractive index, n_a and n_b, along the respective principal layer direction, a and b, perpendicular to the helix axis (Figure 1),

exhibits a circular dichroism $(\epsilon_l - \epsilon_r)$ which is a function of the linear dichroism $(\epsilon_a - \epsilon_b)$ of the layers.[10] Expression (1) holds for a right-handed mesophase and the c.d. is of
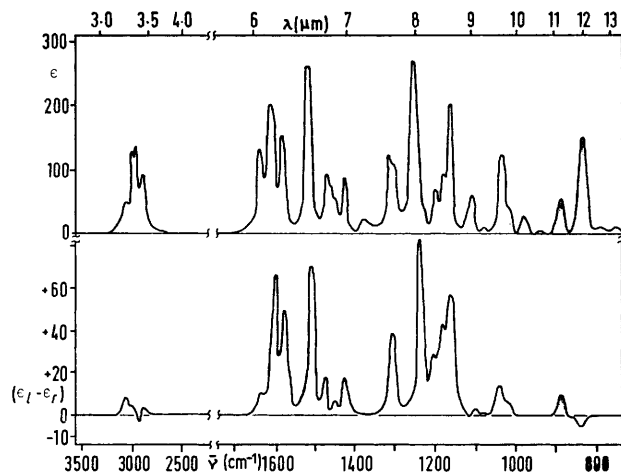

FIGURE 2. *The vibrational absorption (upper spectrum) and circular dichroism (lower spectrum) of compound* (I) *containing* 2% *of* (−)-*menthol measured as* 10—25 *μm film between sodium chloride plates. The intensity scale, ε, refers to the decadic molar extinction coefficient.*

$$(\epsilon_l - \epsilon_r) = (n_a - n_b)(\epsilon_a - \epsilon_b)P/2\lambda \qquad (1$$

opposite sign for a left-handed system. In addition a right-handed mesophase with the mean index of refraction, n, selectively reflects right-circular radiation at the wavelength,[7—9] giving a negative c.d. band. The analogous

$$\lambda_0 = nP \qquad (2)$$

left-handed mesophase giving a corresponding positive c.d. band at λ_0 and in both cases the g-factor has its maximum value, $|2|$.

The molecule (I) has approximately as many vibrational transitions with a- as with b-polarisation, so that the number of positive and negative c.d. bands should be comparable according to (1) if the birefringence has the same sign throughout the i.r. spectrum. The refractive indices, n_a and n_b, undergo a dispersion in the frequency region of a vibrational band with a- and with b-polarisation, respectively, and the mean index, n, is dispersed within the band-width of each vibrational absorption. The observed vibrational c.d. is predominantly positive with minor negative bands at high and at low frequency (Figure 2), suggesting either (i) that the effective birefringence generally changes sign on passing from an a- to a b-polarised band or (ii) that the resonance condition (2) is generally attained within the band-width of each absorption.

The vibrational c.d. has a sign opposite to that of the reflection band at λ_0 in case (i) and the same sign in case (ii). The mesophase studied gives no reflection band in the wavelength region 0·4 to 6 μm, and that band either lies in

an electronic or vibrational absorption region or is too broad to be detected. Strong positive c.d. (g +0·035) is observed in the 300—400 nm electronic absorption region. It is unlikely that the changes of the mean index, n, within an absorption band are sufficient to allow the attainment of the resonance condition (2) at both electronic and vibrational absorption wavelengths, and it is probable that the pre-dominant positive sign of both the electronic and the vibrational c.d. arises from a general change in sign ($n_a - n_b$) when ($\epsilon_a - \epsilon_b$) changes sign in (1). Studies of cholesteric mesophases with detectable reflection bands are on hand.

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