The Optical Activity of Achiral Molecules in a Cholesteric Solvent

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Summary In a cholesteric solvent molybdenum hexacarbonyl and other optically-isotropic molecules give Cotton effects which are due to the differential effective Lorentz radiation field for left and right circular light, arising from the large circular birefringence of the medium.

Following the pioneer studies of Mauguin[1] and of de Vries[2] on the optical rotation of the cholesteric mesophase in transparent wavelength regions, attention has been directed recently to the Cotton effects of cholesteric solutions at absorption frequencies, both electronic[3–5] and vibrational.[6–8] The solute molecules examined hitherto have been anisotropic, structurally and optically, and in the current theory[4,7] of the optical activity of cholesteric solutions it is assumed that the principal axis of the solute molecule has a statistically preferred orientation relative to the director of the local nematic layer. The uniform angle of twist between successive nematic layers making up the cholesteric mesophase produces a helical array of the solute molecule as well as of the solvent molecules. From this model it has been shown[4] that the circular dichroism ($\epsilon_L - \epsilon_R$) of an achiral solute in a right-handed cholesteric solvent with a pitch-length, P, follows equation (1), where $n_{\|}$ and $n_{\perp}$ are refractive

$$(\epsilon_L - \epsilon_R) = (n_{\|} - n_{\perp})\,(\epsilon_{\|} - \epsilon_{\perp})\,\bar{\nu}\,P/2 \qquad (1)$$

indices of the medium parallel and perpendicular, respectively, to the director of a nematic layer, and $\epsilon_{\|}$ and $\epsilon_{\perp}$ are the corresponding extinction coefficients of the solute at the wavelength $\bar{\nu}$.

According to equation (1) achiral molecules of cubic symmetry and other optically-isotopic solutes in a cholesteric solvent should not give Cotton effects at absorption frequencies, owing to the lack of an intrinsic linear dichroism ($\epsilon_{\|} - \epsilon_{\perp}$). However, we find that the octahedral molecule, molybdenum hexacarbonyl, in a cholesteric medium exhibits large Cotton effects in the frequency region of the metal–ligand charge-transfer absorption (Figure), as do

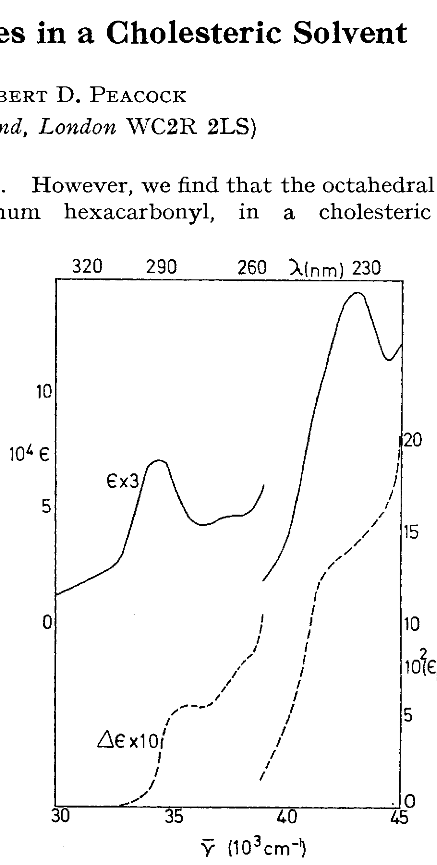

Figure. The absorption spectrum (upper curves) and circular dichroism (lower curves) of molybdenum hexacarbonyl (10^{-2}M) in cholesteryl chloride–cholesteryl nonanoate (40—60 parts by weight) with path lengths 10—30 μm. The cholesteric solvent reflects left circular light at 890 nm, giving a positive pitch-band circular dichroism.

other cubic metal carbonyls. Moreover, solutes which are optically anisotropic give Cotton effects predominantly of one sign in a cholesteric solvent,[3–8] whereas equation (1) indicates that c.d., bands of both signs are expected, the bonds of each set being comparable in number and in total band area over an extended frequency range.

These deviations from relation (1) arise from the large circular birefringence of cholesteric solvents. The absorption of left and right circular light by a solute molecule depends not only upon the dipole strength of the transition considered for the two circular components, these strengths being necessarily equal for an achiral molecule, but also upon the effective radiation field strength of the two circular components, which generally differ in chiral solvents. An application of the Lorentz correction term, $[(n^2 + 2)/3]$, for the effective electric field strength[9] in a medium of refractive index n, indicates that the c.d. of a species in solution $(\epsilon_L - \epsilon_R)_S$ is related to the corresponding vapour phase c.d. absorption $(\epsilon_L - \epsilon_R)_V$ by equation (2) where n_L

$$(\epsilon_L - \epsilon_R)_S = [(n^2 + 2)/3](\epsilon_L - \epsilon_R)_V + 2(n_L - n_R)\bar{\epsilon}_S/(\bar{n}^2 + 2) \qquad (2)$$

and n_R are refractive indices of the solvent for left and right circular light, respectively, $\bar{n}$ being the mean refractive index of the solvent, and $\bar{\epsilon}_S$ is the mean extinction coefficient of the solute. Thus an achiral molecule, for which the vapour phase c.d. is zero, exhibits c.d. absorption in a chiral solvent with a dissymmetry factor, g, given by equation (3). With present-day instrumentation, measuring g-factors down to *ca.* 10^{-5}, the c.d. of an achiral molecule,

$$g = (\epsilon_L - \epsilon_R)_S/\bar{\epsilon}_S = 2(n_L - n_R)/(\bar{n}^2 + 2) \qquad (3)$$

from equation (3), is accessible for solutions in a chiral solvent with a rotation of approximately one radian per cm or greater. Such rotations are rare for isotropic liquids but are common for cholesteric solvents.

The frequency dependence of the c.d. absorption of an achiral solute in a cholesteric solvent is obtained from equation (3) and the expression of de Vries[2] for the optical rotatory dispersion of a cholesteric system. For a cholesteric solvent with a negative pitch c.d., reflecting right-circular light at the pitch-band wavenumber, $\bar{\nu}_0 = [1/(P\bar{n})]$, the c.d. absorption of an achiral solute at the wavenumber, $\bar{\nu}$ is given by equation (4). In mixtures of cholesteryl

$$(\epsilon_L - \epsilon_R)_S/\bar{\epsilon}_S = (n_\parallel - n_\perp)^2 P(\bar{\nu})^3/[2(\bar{\nu}^2 - \bar{\nu}_0^2)(\bar{n}^2 + 2)] \qquad (4)$$

chloride and cholesteryl esters similar to those used in the present work the linear birefringence $(n_\parallel - n_\perp)$ and the mean refractive index $\bar{n}$ have values[10] in the region of 0·055 and of 1·50, respectively, over the visible wavelength range. These values give through equation (4) a theoretical g-factor of $-0{\cdot}8 \times 10^{-3}$ for an achiral and optically-isotropic solute absorbing at 35 kK in a cholesteric solvent which reflects left light at the pitch-band wavenumber, 11·2 kK. The g-factors of -2×10^{-3} and -10^{-2}, respectively, are observed for the 35 and the 43 kK bands of molybdenum hexacarbonyl in the cholesteric medium studied (Figure). The linear birefringence of the cholesteric solvent, appearing as its square in equation (4), is expected to be substantially larger at 35 and, more particularly, at 43 kK than in the visible region. Furthermore, that birefringence is no longer wholly real and becomes complex from 40 kK to higher frequencies with the onset of solvent absorption. It is expected additionally from equation (4) that the c.d. absorption of an achiral solute is of opposite sign to that of the pitch band of the cholesteric solvent if $\bar{\nu} > \bar{\nu}_0$ or of the same sign if the converse wavenumber inequality obtains. This expectation is exemplified without exception by the sign of the predominant c.d. absorption bands exhibited over an extended wavelength range by achiral but anisotropic solutes in a cholesteric solvent[3–5] or by a neat cholesteric mesophase.[6–8] Thus equation (4) is general, applying to both isotropic and anisotropic solutes in a cholesteric solvent, but in the latter case the optical properties specified by equation (1) are superposed.

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