Table IV. Recommended Heats of Formation for Fluorine-Substituted Carbonium Ions and Related Thermochemical Data

R^+	$\Delta H_f°_{298}$ (R^+)[a]	$\Delta H_f°_{298}$ (R)[a]	IP(R)[b]	$D(R^+$-$H^-)$[a,g]	$D(R^+$-$F^-)$[a,g]
$CH_3CH_2^+$	218.9	25.7[c]	8.38[c]	272.5	220.5
CH_3CHF^+	165.9[d]	−17.0[e]	7.93	262.2	224.3
$CH_3CF_2^+$	108.8[d]	−73.8[e]	7.92	261.9	225.7
$(CH_3)_2CH^+$	191.7	17.6[c]	7.55[c]	249.9	199.4
$(CH_3)_2CF^+$	138.0[d]	−26.6[f]	7.14	240.4	206.5

[a] Data in kcal/mol. [b] Ionization potentials in eV. [c] F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970). [d] Estimated uncertainty ±3 kcal/mol (see text). [e] $D(CH_3CHF\text{-}H) \simeq D(CH_3CF_2\text{-}H) \simeq D(CH_3CH_2\text{-}H) = 98.0$ kcal/mol assumed to calculate $\Delta H_f°_{298}(R)$. [f] $D[(CH_3)_2CF\text{-}H] \simeq D[(CH_3)_2CH\text{-}H] = 94.5$ kcal/mol assumed to calculate $\Delta H_f°_{298}[(CH_3)_2CF]$. [g] Heterolytic bond dissociation energies $D(R^+\text{-}X^-) = \Delta H_f°_{298}(R^+) + \Delta H_f°_{298}(X^-) - \Delta H_f°_{298}(RX)$ for X = H, F.

a thermal rate constant of $k = 4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [25,26] For reaction 8 to be exothermic it is required that

$$CH_3CHF^+ + C_2H_5F \longrightarrow C_2H_5^+ + CH_3CHF_2 \qquad (8)$$

$\Delta H_f°_{298}(CH_3CHF^+) \geq 162.1$ kcal/mol, which is also consistent with the derived value of 165.9 kcal/mol.

Recommended heats of formation for the various fluorine-substituted ions considered in this study are summarized in Table IV. Although differences in thermochemical properties are more accurately determined in several instances, it appears reasonable to assign uncertainties of ±3 kcal/mol to the derived heats of formation.

Included in Table IV are several related thermochemical properties. As is observed in the methyl series,[2,3] fluorine substitution on the carbonium ion center results in a reduction of the ionization potential of the corresponding radical. In addition, fluorine substitution at the carbonium ion center consistently results in an increase in the $D(R^+\text{-}F^-)$ and a decrease in the $D(R^+\text{-}H^-)$ heterolytic bond dissociation energies. The origin of this phenomenon and its interesting consequences have been previously discussed.[2,3,16]

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Extrinsic Circular Dichroism in Twisted Nematic Mesophases

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Abstract: Extrinsic wavelength dependent circular dichroism (CD) has been observed in twisted nematic mesophases produced by placing an achiral nematic liquid crystalline material between rubbed surfaces held at an angle between 0 and 90°. The extrinsic CD was extracted from the combination of linear dichroism (LD) and CD by summing signal intensities on a Cary 61 CD spectropolarimeter taken at cell rotation angles (normal to the light beam) of 90° with respect to each other. The sign of the CD is dependent on the chirality of the twist as well as the polarization of the optical transition dipole moment of the matrix or aligned solute molecules. Nematic mesophases between rubbed surfaces placed at 90° relative to each other produce CD of either positive or negative sign due to the apparently equal probability of forming left- or right-handed helical structures. It is concluded from this investigation that the twisted nematic mesophase is cholesteric in nature.

The prebiotic generation of optical activity, i.e., a racemic mixture enriched in one enantiomer, is not fully understood.[1] Recently we have reported an asymmetric synthesis in an anisotropic cholesteric liquid crystal solvent[2] in which an achiral reactant was thermally rearranged to a chiral product. Several other processes for the creation of chiral species have been

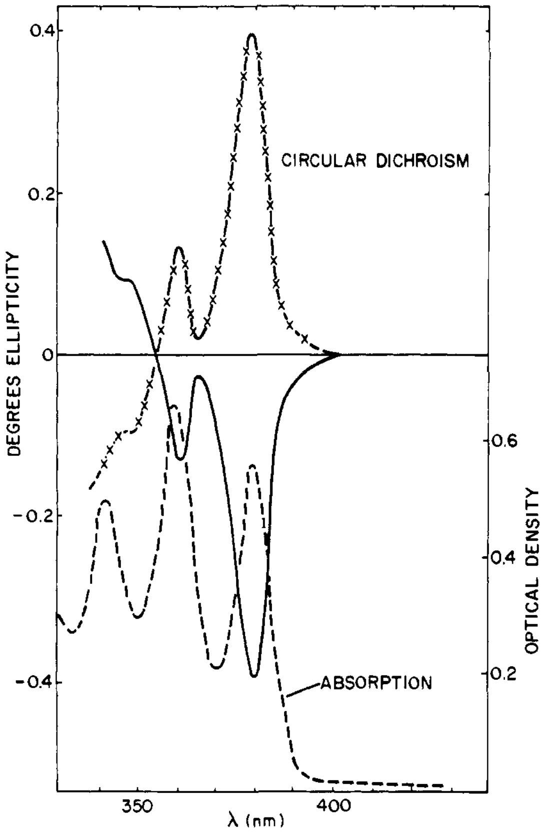
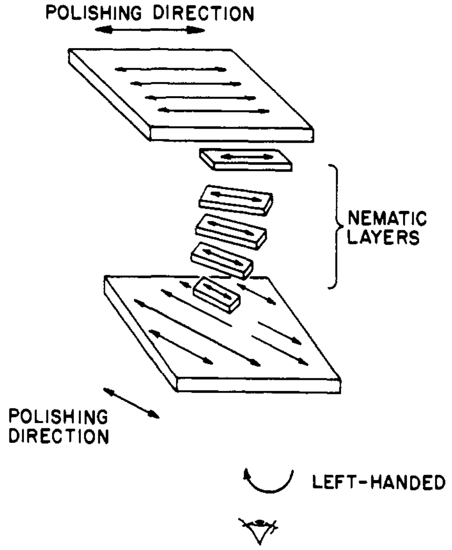


Figure 1. Absorption and circular dichroism (θ_{real}) spectra of anthracene (1 wt %) in 1:1 (wt %) *p*-cyanophenyl *p*-butylbenzoate/*p*-cyanophenyl *p*-heptylbenzoate (24 μ film; 45° twist): (—) left handed; (-X-) right handed.

postulated including effects of circularly polarized light.[1] However, one must first have a method of producing circularly polarized light (CPL). For this reason, the production of CPL using achiral systems would appear relevant to the origin of optical activity. Achiral aggregated molecules, e.g., liquid crystalline mesophases, normally display only *linear* (orientation dependent) birefringence and dichroism (LD). For the production of circular birefringence and dichroism (CD) in these systems a chiral perturbation is required.[3,4] The close relationship between achiral nematic mesophases and chiral cholesteric systems is especially interesting in this regard and is the focal point of this paper.

The "Grandjean" (planar) texture[5] of the cholesteric mesophase exhibits enormous wavelength dependent circular birefringence (several hundred thousand degrees/mm) and dichroism (reflective[6] and absorptive[7]) due to the presence of a macroscopic helical structure. Achiral nematic mesophases, on the other hand, display only linear birefringence and dichroism when unperturbed. They may, however, be converted into a cholesteric system simply by the addition of small quantities of a chiral solute (~1 wt %) or by introduction of any other dissymmetric perturbation so as to alter the delicate balance between helical and nonhelical aggregated structures.[3] In fact, the chiral mechanical perturbation produced by placing a nematic material between rubbed surfaces[8] which are at some angle between 0 and 90° is sufficient to produce a helically structured mesophase.[9] The rubbing or polishing process produces a grooved surface which causes molecular alignment along the rubbing or polishing direction.[8] A schematic representation of the 45° mechanically twisted mesophase is described below. The alignment of molecules within the bulk are controlled by neighboring molecules oriented at the two surfaces.



This mechanically induced chiral system is termed the twisted nematic mesophase. The pitch[10] of the helical structure is defined by an angle between the two substrates as well as by sample thickness.[9] Wavelength *independent* optical rotation of plane polarized light (for $\lambda \ll$ cell thickness) has been observed in twisted nematic mesophases which depends on the angle of twist between the aligning surfaces[9,11] as well as cell orientation with respect to the incoming linearly polarized light beam, e.g., a ~90° twisted mesophase produces optical rotation of ~90°. This wavelength independent optical rotation has been attributed to the linear birefringence of the twisted nematic mesophase.[11]

We report here the observation of wavelength dependent extrinsic circular dichroism (CD) in twisted nematic mesophases. The sign of the CD is dependent on the chirality of the twist as well as the polarization of the optical transition dipole moment of the matrix or aligned solute molecules, while the CD magnitude is dependent on the degree of twist.

Experimental Section

Circular dichroism spectra were run on a Cary 61 CD spectropolarimeter. Samples consisted of thin films of the liquid crystal between 1-in. square ⅛-in. thick quartz plates using a 24μ Mylar spacer. The plates were placed together with a well-defined angle between the polishing directions. Absorption spectra were taken on a Cary 15 spectropolarimeter.

To ensure proper molecular alignment new quartz disks were polished carefully by making ca. 10 passes in a single direction with a piece of soft cotton, rinsed with distilled water and acetone prior to drying in an oven set at 100 °C. The rubbing procedure provides a grooved surface which stabilizes molecular alignment along the direction of the grooves.[8,12] The optical cell for the CD studies consisted of a thin film of the mesophase between quartz plates within a circular brass unit which allowed convenient rotation of cells normal to the incoming light beam.

Materials. Anthracene employed in this study was purchased from Princeton Organics, Princeton, N.J., and was of Prinz quality (99.999 mol % purity). *p*-Cyanophenyl *p*-butylbenzoate [(**1**), 66.5° monotropic] and *p*-cyanophenyl *p*-heptylbenzoate [(**2**), 43-57° nematic] were purchased from the Aldrich Chemical Co. and recrystallized twice from hexane before use. A 1:1 (wt %) mixture of **1** and **2**, which formed a supercooled nematic mesophase, was employed throughout this study as the achiral mesophase of choice. Cholesteryl oleyl carbonate was purchased from Eastman Kodak Co., Rochester, N.Y., and used without any further purification.

Discussion

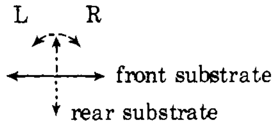
Within the wavelength region of the optical transitions of the liquid crystal or aligned solute molecules, with the twisted nematic structure, signals (θ_{obsd}) measured on a Cary 61 CD spectropolarimeter are due to a combination of CD (θ_{real}) and LD (θ_{LD}) as described in eq 1. These signals are also modified by the linear birefringence (LB) of the sample. However, linear dichroism and birefringence effects can be made to cancel by summing signal intensities taken at cell rotation angles (normal to the light beam) of 90° with respect to each other.[13] The real CD was measured by using the relationship shown below in eq 2.[13] The absolute values of the rotation angles are not important to the extraction of the CD intensity, it is only important that they be 90° apart.

$$\theta_{\mathrm{obsd}} = \theta_{\mathrm{real}} + \theta_{\mathrm{LD}} \quad (1)$$

$$\theta_{\mathrm{real}} = \tfrac{1}{2}[\delta\theta(0°,90°) + \delta\theta(-30°,60°)] \quad (2)$$

Figure 1 presents the CD (θ_{real}) and absorption spectra of anthracene between 330 and 400 nm in the cyanobenzoate nematic mesophase with a left- and a right-handed 45° twist. Anthracene serves as a probe to the internal structure of the mesophase by aligning its long molecular axis parallel to the local optic axis of the nematic-like layer.[14] The transversely polarized (short axis in-plane) optical transitions at 360 and 380 nm exhibit negative and positive CD in the left- and right-handed twisted nematic mesophase, respectively. The intensity of the extrinsic CD of anthracene increases with the angle of twist of the mesophase and changes sign with the chirality of twist with the exception of the 90° twisted sample. When the aligning surfaces are placed parallel, i.e., 0° twist, only linear dichroism exists as demonstrated by the canceling of the observed CD signals recorded at cell angles 90° relative to each other. CD signs in the twisted nematic mesophases are entirely consistent with that previously found for anthracene in left- and right-handed helical cholesteric mesophases[14] where the wavelength of absorption is shorter than the pitch of the helix.

However, when the aligning surfaces are at 90° there are two equally probable twist directions, i.e., left and right handed. Areas of reverse twist within this mesophase have been observed microscopically between crossed polarizers.[15,16] The 90° twisted mesophase exhibits CD of approximately the same intensity as for the 45° twist sample. However, the CD signals in the 90° twist sample disappear upon heating of the mesophase into the isotropic phase and reappear upon cooling with either a positive or negative sign in an unpredictable manner. This behavior appears to be a consequence of the zero free energy difference between the enantiomeric twisted mesophases formed when the twist angle is precisely 90° as well as reflecting the chirality of the predominant phase in the area being monitored.



L=left-handed; R=right-handed

A large pitch right-handed helical cholesteric mesophase ($P \cong 100\ \mu$)[10] was formed by the addition of cholesteryl oleyl carbonate (0.12 wt %) to the nematic mixture used throughout the study. Using either a *single* rubbed surface or unrubbed surfaces and cell thickness of ~12 μ, a mesophase structurally analogous to the right-handed 45° twisted nematic mesophase was produced. The extrinsic CD, LD, and linear birefringence of these two mesophases were virtually identical.

Conclusion

In summary, wavelength dependent extrinsic circular dichroism has been observed within the electronic transitions of achiral molecules ordered in twisted nematic mesophases. The CD sign is entirely consistent with previous investigations of liquid crystal induced circular dichroism (LCICD) in cholesteric systems.[14] A simple mechanical chiral perturbation results in the appearance of CD in aggregated achiral mesophases completely analogous to cholesteric mesophases produced by chiral solute addition to nematics and by sterol ester systems. From these investiations we conclude that the twisted nematic mesophase is cholesteric in nature. We also feel that circularly polarized light produced from achiral aggregated systems in the manner analogous to that described above may possibly have been important in the creation of chiral species by means of a photochemical resolution process.

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