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Mechanisms for the Effect of Electric and Magnetic

Fields on Biological Systems

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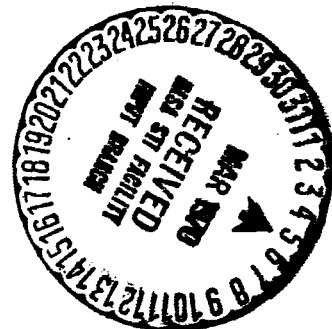
Introduction

We continued our investigation of electric and magnetic field effects on the structure and properties of cholesteric liquid crystals, and the report consists of preprints of the following manuscripts which adequately summarize our work.

(1) "AC Field Induced Cholesteric-Nematic Phase Transitions", H. Baessler and M. M. Labes, J. Chem. Phys.

(2) "The Absence of Helical Inversion in Single Component Cholesteric Liquid Crystals", H. Baessler, P. A. G. Malya, W. R. Nes and M. M. Labes, Mol. Cryst. and Liq. Cryst.

(3) "Helical Twisting Power of Steroidal Solutes in Cholesteric Mesophases", H. Baessler and M. M. Labes, J. Chem. Phys.

(4) "Determination of the Pitch of a Cholesteric Liquid Crystal by Infrared Transmission Measurements", H. Baessler and M. M. Labes, Mol. Cryst. and Liq. Cryst.

Alternating-Current-Field Induced Cholesteric-Nematic Phase

Transitions

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In order to determine whether interaction between the permanent or the induced molecular dipole moments of a cholesteric liquid crystal and an applied electric field is responsible for inducing a transition to a nematic phase, ac-field measurements were performed. In a mixture of cholesteryl chloride and cholesteryl myristate, phase transitions can be induced by an ac field of a frequency up to a threshold value f_{pt}. f_{pt} is approximately equal to the relaxation frequency for rotation of cholesteryl chloride molecules around a short molecular axis which has recently been determined by dielectric measurements. A relation between the rms field and f_{pt} is derived and experimentally verified. The absence of ferroelectric ordering in the induced and aligned nematic phase is demonstrated.

Introduction

A cholesteric liquid crystalline structure consists of optically anisotropic monomolecular layers, subsequent layers being twisted by a small angle. The long axes of the molecules are approximately parallel to the plane of the layers constituting the helical structure. Stability of the structure requires that the free energy of the system is a minimum with respect to any phase change, and application of an electric or magnetic field to an ordered liquid crystal changes the free energy in a definite way. If the anisotropy of the structure is such that the long molecular axes tend to be parallel to an applied field, the twisted cholesteric structure becomes unstable above a critical field and a nematic phase can be induced,[1,2] both if the field is applied parallel or perpendicular to the helix axis. The driving force to accomplish a phase transition is the torque acting on the structure. It results from interaction between an electric field and the permanent or induced molecular dipole moments or from interaction between a magnetic field and the induced magnetic moments.

The present paper is concerned with the relative contribution of permanent and induced electric moments in electric field induced cholesteric-nematic phase transitions. Previous dc-measurements had been interpreted in terms of field-permanent dipole interaction.[3] This assignment has, however, been questioned recently by Wysocki and

Haas.[4] Therefore ac-field experiments were performed to clarify the situation: if interaction between the field and the permanent dipoles is of major importance, there should be an upper frequency limit for the exciting ac field which should approximately coincide with the relaxation frequency of the dipoles involved.

Theoretical Background

The change in the free energy density of a cholesteric liquid crystal being converted to nematic by an electric field F is

$$E = E(k_{11}, k_{22}, k_{33}, Z) + E_F \qquad (1)$$

where $E_F = \Delta\epsilon F^2/8\pi$ is the difference in electrostatic energy and $\Delta\epsilon$ is the difference in the dielectric constant when passing from the cholesteric to the nematic structure. k_{11}, k_{22}, k_{33} are the elastic constants for splay, torsional and bending strain. Z is the pitch of the undisturbed helix. $\Delta\epsilon$ depends on whether the field is applied parallel ($\Delta\epsilon_\parallel$) or perpendicular ($\Delta\epsilon_\perp$) to the direction of the helix axis which shall be characterized by a unit vector $\vec{h}$. Phase transition can only take place if E_F exceeds a critical value E_c:

$$\Delta\epsilon F^2/8\pi \gtreqless E_c \qquad (2)$$

De Gennes[1] and Meyer[2] have derived the following expressions for the critical energy E_c using Frank's theory[5] for the elastic energy

- 2 -

stored in the cholesteric mesophase:

$$E_c = (2\pi^2/z^2)\ (k_{22}{}^2/k_{33}) \quad \text{for } \vec{F} \parallel \vec{h} \qquad (3)$$

$$E_c = \pi^4 k_{22}/8z^2 \qquad\qquad \text{for } \vec{F} \perp \vec{h} \qquad (4)$$

The energy condition of eq. 2 requires $\Delta\varepsilon > 0$. In principle this can be achieved in three ways:

(1) $\Delta\varepsilon$ can be split into two parts arising from the anisotropy of both the dipolar and the electronic polarizabilities: $\Delta\varepsilon = \Delta\varepsilon_\mu + \Delta\varepsilon_{el}$. It can be shown that $\Delta\varepsilon_{el} > 0$ is always fulfilled with a cholesteric-nematic phase-transition. From the molecular optical anisotropy of the mesophase constituting rodlike molecules, it follows that a cholesteric liquid crystal behaves optically negative with an optical axis parallel to the direction $\vec{h}$ of the helix axis, wherea., a nematic liquid crystal is optically positive with an optical axis parallel to the preferred direction cf the long molecular axes, defined by a unit vector $\vec{L}$. Going from a cholesteric structure with $\vec{h} \parallel \vec{F}$ and $\vec{L}$ approximately $\perp \vec{F}$ to a nematic structure with $\vec{L} \parallel \vec{F}$ therefore means an increase in the refractive index and, because of the relation $\varepsilon_{el} = n^2$, also an increase of ε_{el} in a direction $\parallel F$. The change of ε_{el} is given by $\Delta\varepsilon_{el} = n^2 - (n + 1/2\Delta n)^2 \approx n$ where Δn is the anisotropy of the refractive index. For non-aromatic compounds forming a cholesteric phase $\Delta n = \Delta\varepsilon_{el} \approx 0.05$[6,7] which may be compared to a dielectric anisotropy of 2 derived from experiments on dc-field-induced phase transitions. This means that in principle cholesteric-nematic phase transitions should be

- 3 -

observable with ac fields up to optical frequencies interacting with the induced electric moments. However, the threshold field values should be about one order of magnitude higher than those observed with dc-fields.

(2) Usually the constituting molecules possess a permanent dipole moment with a component $\vec{\mu}_L$ parallel to the long molecular axis. If in the induced nematic phase the dipole components $\vec{\mu}_L$ would align parallel to each other thus forming a ferroelectric structure, the dielectric constant ϵ_{nem}, and therefore $\Delta\epsilon$, should reach very high values.[8] The response time of the structure to a reversal of the aligning field should be relatively long - of the order of seconds - because it involves macroscopic reorientation. Consequently cholesteric-nematic phase transitions involving ferroelectric ordering should be induced most efficiently with dc or ac-fields of very low frequency and a relatively small amplitude.

(3) If the molecules have a dipole moment with a major component directed along the long molecular axis, but the individual dipoles are assumed to be independent of each other, then the low frequency dielectric constant is determined by the dipolar polarizability $\alpha = \mu_{\parallel}^2 /kT$ where $\mu_{\parallel}$ is the dipole component along the ac-field direction. Rotation of $\vec{L}$ towards the field direction, which is what occurs during a phase transition, therefore causes an increase of $\mu_{\parallel}$. Hence the change in the dielectric constant is $\Delta\epsilon = \epsilon_{nem} - \epsilon_{chol} > 0$. $\Delta\epsilon$ includes also the change in electronic polarizability: $\Delta\epsilon = \Delta\epsilon_{\mu} + \Delta\epsilon_{el}$. However, at low

- 4 -

frequencies the dipolar part dominates: $\Delta\varepsilon_\mu \gg \Delta\varepsilon_{el}$. The dielectric constant ε'_{ncm} of the aligned nematic phase is independent of F as long as F exceeds the critical F_c defined by eq. 2. The important feature, however, is that according to the Debye-Langevin theory the distribution of dipoles $\mu_\shortparallel$ among the two allowed positions parallel and antiparallel to the field is given by Boltzmann's law. The difference in number is:

$$\Delta N = 1/2N[1 - \exp(-2\mu F/kT)] \approx N\mu F/kT \qquad (5)$$

where N is the dipole density. For $\mu = 1$ D, $F = 30$ kVcm^{-1} and $T = 40°$ one obtains $\Delta N/N = 2.3 \times 10^{-3}$. This means that upon reversal of the aligning field only the fraction $\Delta N/N$ of the molecules is required to change direction in order to preserve the energetic condition for the stability of the induced nematic phase. The macroscopic orientation pattern of the phase should remain unchanged.

The response of a cholesteric structure with $\vec{\mu} \shortparallel \vec{L}$ to an ac field should therefore be the same as the response to a dc-field except for two cases: (a) if the frequency is too low, in practice below 1 c/s, the material can relax to the cholesteric ground state while the field is oscillating between its + and - peak values; (b) if the frequency exceeds the relaxation frequency for dipole rotation, the dipoles can no longer follow. Consequently $\Delta\varepsilon_\mu$ decreases as a function of f, and according to eq. 2 the critical rms field has to be increased. Assuming that the dipole relaxation frequency f_r is the

same in the cholesteric and induced nematic phase, the decrease of $\Delta\varepsilon_\mu$ can be expressed in terms of Debye's theory:

$$\Delta\varepsilon_\mu(f) = \Delta\varepsilon_{\mu o} \, [1 + (f/f_r)^2]^{-1} \qquad (6)$$

From eq. 2 it follows that

$$[F_{c,ac}(f = f_{pt})/F_{c,dc}]^2 = \Delta\varepsilon_{\mu o}/\Delta\varepsilon_\mu \, (f = f_{pt}) \qquad (7)$$

Insertion of eq. 6 yields the dependence of the critical rms field $F_{c,ac}$ on the frequency f_{pt} above which a phase transition can no longer occur:

$$F_{c,ac}{}^2 = F_{c,dc}{}^2 \, [1 + (f_{pt}/f_r)^2] \qquad (8)$$

Measurement of $F_{c,ac}$ as a function of the frequency f_{pt} should therefore yield the values for the dipole relaxation frequency f_r and the critical dc-transition field $F_{c,dc}$. Since both values[3,8] have been determined recently, the experiment should decide unambiguously whether or not interaction of the electric field with the permanent molecular dipole moments is the major driving force for the cholesteric-nematic phase transition.

Experimental and Results

Samples of a 1.75:1.00 weight mixture of cholesteryl chloride and myristate were sandwiched between quartz discs coated with tin oxide or evaporated semitransparent gold electrodes and kept at a

distance of 10μ by a mylar spacer.[3] Two Hewlett Packard audio

oscillators were used as ac-voltage supplies: type 200 CD with a

maximum rms output of 23 volts in the frequency range 0.5-600 KC

and type 201 C with a maximum rms voltage of 55 volts at frequencies

below 22 KC.

The cholesteric-nematic phase transition was detected

optically by monitoring the optical rotatory power (OR) of the choles-

teric phase, since the optical activity vanishes if the cholesteric

phase is converted to nematic.[6] For this purpose, sample and sample

holder were inserted into a modified tube of a Rudolph polarimeter.

The experimental procedure was as follows: the sample was set at a

preselected constant temperature. Then a constant rms field F_{ac} of

a frequency f above the relaxation frequency of the cholesteryl chloride

molecules was applied. Finally, f was reduced in a stepwise manner

until the OR had vanished indicating that the phase transition had

occurred. The run was repeated at several F_{ac}-values. The insert in

Fig. 1 gives an example of the dependence of the rotation angle on the

frequency of the ac field. The critical frequency f_{pt} is defined by

the intersection of the extrapolated main portion of the OR(f)-curve

with the base line. Upon re-increasing the frequency a slight hysteresis

effect is observed, i.e. re-establishment of the cholesteric phase

occurs at a frequency slightly higher than f_{pt} (usually about 1.3 f_{pt}).

A plot of the square of the rms field $F_{c,ac}$ which is

sufficient to induce a phase transition at the frequency f_{pt} versus

f_{pt}^2 gives a straight line as predicted by eq. 8 (see Fig. 1). It is, in particular, noteworthy that the extrapolation of the ac-data to $f \to 0$ coincides with the direct determination of the dc transition field. This rules out any possible increase of the dielectric constant, and hence the electrostatic energy, at very low frequencies, thus disproving the existence of any ferroelectric ordering in the aligned nematic phase. It also demonstrates that $F_{c,dc}$ is not affected by any electrode polarization effects which could reduce the field in the bulk. They should certainly vanish for $f \gtrsim 10^2$ c/s thus yielding

$$\lim_{f \to o} F_{c,ac} < F_{c,dc}.$$

From the slope of the straight line in Fig. 1 the frequency f_r can be determined. At $T = 29°$, one obtains $f_r = 11.7 \pm 0.5$ KC. This value is identical with the relaxation frequency for rotation of the cholesteryl chloride molecules around a short molecular axis, which has recently been determined from the frequency dependence of the dielectric constant[9] to be 11.3 ± 0.5 KC at that temperature. The coincidence between the relaxation frequency f_r, determining the characteristics of an ac field induced phase transition, and the dipole relaxation frequency at various temperatures is demonstrated in Fig. 2. For the sake of simplicity, some data have been determined by direct microscopic observation of the phase transition which is, however, less accurate.

Concluding Remarks

The present results confirm our previous assumption[3,9]

- 8 -

that the energy required to induce a cholesteric-nematic phase transition in CM involves interaction between the electric field and the permanent molecular dipoles. This interaction causes redistribution of the cholesteryl chloride molecules which have permanent dipole moments $\vec{\mu}_c$ along the long molecular axis. The redistribution is such that all long molecular axes tend to be parallel to the field, and a Boltzmann distribution for $\vec{\mu}_c$ being parallel or antiparallel to the field is established. The time required to build up the new structure after application of an ac field is of the order of seconds since macroscopic aligning processes are involved. The threshold ac frequency above which a phase transition can no longer be induced, is, however, independent of this time. It is solely determined by the relaxation frequency for dipole rotation which enters the expression for the dielectric anisotropy. The present results are felt to apply to all systems in which cholesteric-nematic phase transitions have been thus far observed,[10,11] since they all consist of a mixture of a cholesteryl ester with a cholesteryl halide: the dipole moment of the halide produces the right sign of the dielectric anisotropy, whereas the ester serves to compensate the helical structure thus increasing the pitch and lowering the transition field. Phase transitions occurring at much higher frequencies than the dipole relaxation frequency of the halide molecules should in principle be possible by interaction between the field and the induced molecular moments, but they should require transition fields which are about one order of magnitude higher because of the small anisotropy of the molecular electronic polarizability.

Ac-fields with $f < f_r$ and $F_{ac} < F_{c,ac}$ should be able to cause conical helical perturbation as has been found with dc fields.[2,3] This includes the possibility of a periodic modulation of the birefringence as observed by Wysocki and Adams.[4] The frequency of these modulations must be twice the ac frequency because of the non polar liquid crystalline structure which makes both ac-half waves equally effective.

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Figure Captions

Figure 1: Plot of the square of the rms field versus the square of the critical frequency f_{pt} for inducing a cholesteric-nematic phase transition, $T = 29°$. Insert: dependence of the optical rotation angle on the frequency, sample thickness 10μ, rms field $F_{ac} = 23$ KVcm^{-1}, wavelength of the analyzing light 5890 Å.

Figure 2: Comparison between relaxation frequency f_r determined from equation 8 (open circles) and the temperature dependence of dipole relaxation corresponding to rotation of cholesteryl chloride around a short molecular axis in the (1) cholesteric phase and (2) induced nematic phase of CM.
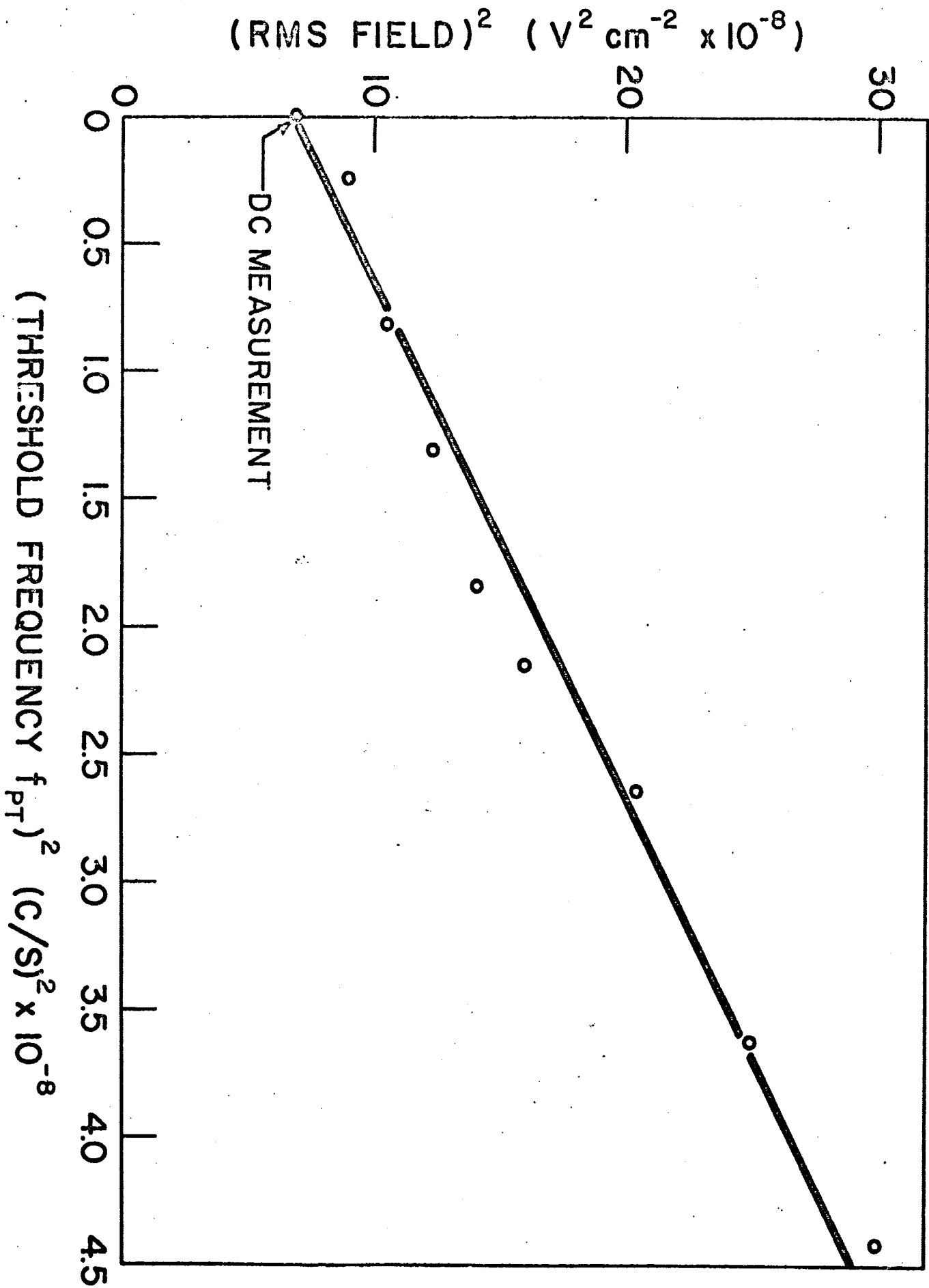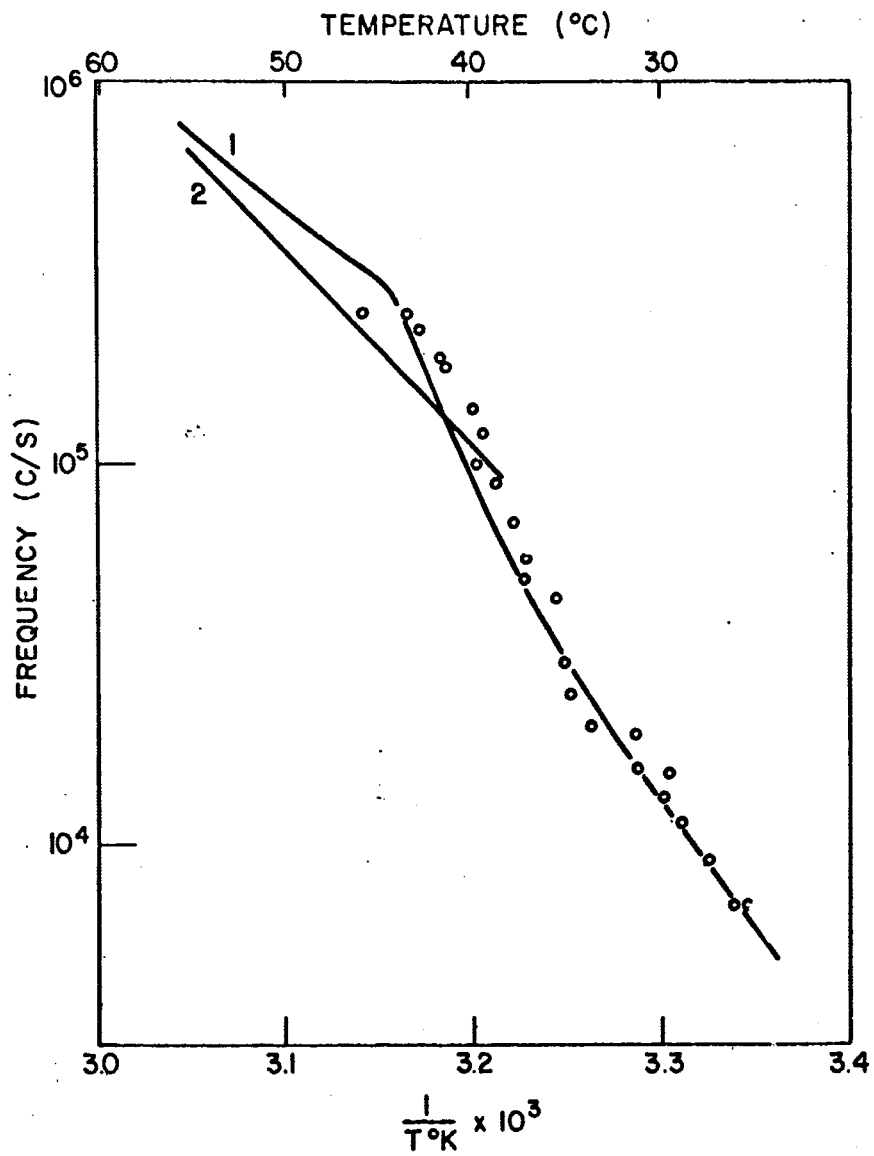
Figure 1

Figure 2

The Absence of Helical Inversion in Single Component Cholesteric

Liquid Crystals[*]

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Since a thermally induced helical inversion has been observed

in cholesteryl 2-(2 ethoxyethoxy) ethyl carbonate (CEC), it has been

the view that compensation of the helical structure of cholesteric

liquid crystals does not require the presence of two compounds which

separately form a right and a left handed helix. The present investiga-

tion demonstrates that the material used in the previous investigation

was probably a compensated mixture because it contained an impurity in

a rather high concentration. Pure CEC forms a right handed helix with

a pitch of 6000 $\overset{o}{A}$ at room temperature, and with no indication of a

thermally induced helical inversion. It is further shown that in general

the sense of the helical screw is not necessarily identical with the sign

of the optical rotation of the constituent molecules.

Introduction

In cholesteric liquid crystals formed from one component, the pitch of the helix can be varied thermally. The sense of the helical screw, however, which is often assumed to correspond to the sign of the optical rotation of the constituent molecules,[1] remains unchanged. The only system which has been reported to _not_ behave in this manner is cholesteryl 2-(2 ethoxyethoxy) ethyl carbonate (CEC), in which an inversion of sign was observed at approximately 30°.[2] Normally such a thermally induced inversion is only found in compensated mixtures of compounds separately forming a right and a left handed helix such as cholesteryl chloride-cholesteryl myristate in a 1.75 to 1 ratio where it occurs at approximately 42°.[3] The problem is of importance to an understanding of the cholesteric structure, and the possibility of impurity effects being responsible for the behavior of CEC had not been eliminated.

The possibility that impurities might play an important role in CEC was suggested by a paper by Durand and Lee[4] reporting that CEC contains crystalline leaflets which gradually melt above room temperature and which are responsible for second harmonic generation of light.[5] These authors, however, claimed that the leaflets were _not_ impurities but ordinary crystallites of CEC. The present investigation shows that this is not the case: the crystallites consist in the main of an impurity which is also responsible for the observation of helical compensation.

- 1 -

Purification of CEC

CEC was obtained from the same source (Distillation Products Ind.) as that which Durand and Lee[2,4] had used. It was found by visual examination that it consists of a viscous liquid and a small amount of crystalline material. As a thin film, the well stirred mixture showed strong carbonyl absorption at 5.77μ and weak carbonyl absorption at 5.66μ. When submitted to thin layer chromatography (silica gel G, acetone in methylene chloride, 1/9, v/v, visualized with I_2 vapor), several components were observed with R_F values of 0.27, 0.51 and 0.81-0.89.

Another sample of CEC (200 mg) was chromatographed on a column of (20 g) silica gel G deactivated with 3% water (w/v). Fractions of 50 ml each were collected using n-hexane-benzene, 8/2 (fractions 1-4), n-hexane-benzene, 1/1 (fractions 5-9), benzene (fractions 10-14), benzene-ether, 3/1 (fractions 15-19), benzene-ether, 1/1 (fractions 20-24), and ether (fractions 25-29). Fractions 2-4 yielded a colorless crystalline material; fractions 11-14 contained a substance with the same R_F as cholesterol; and fraction 15 contained the oily ester (142 mg). Repetition of the chromatography with an additional 400 mg of crude ester yielded an additional 285 mg of pure ester. The R_F of the pure ester was 0.57, and as a thin film on sodium chloride it showed a single peak for carbonyl absorption at 5.75μ(Fig. 1A).

The major impurity was collected as fractions 2-4(45 mg from 200 mg CEC), and melted at 152-161°, with softening at 99°. Its infrared spectrum showed two carbonyl peaks at 5.66 and 5.77μ (Fig. 1B). It

(2.0 mg) was not soluble in 50 ml boiling ethanol. It was, however, soluble in cyclohexane, and in this solvent exhibited no absorption in the UV. These data exclude the possibility of hydrocarbon impurities which could arise during preparation of the ester, viz., Δ^6-3,5-cyclo-cholestene, $\Delta^{3,5}$-cholestadiene, and $\Delta^{4,6}$-cholestadiene. A possible structure is dicholesteryl carbonate, m.p.[6] 176°, clears at 248°, but insufficient data are available in the literature to make an exact comparison.[7] This impurity is clearly present in commercial CEC as evidenced by the infrared spectra (Fig. 1C). Its concentration is so high that it precipitates at room temperature and forms crystallites floating in the bulk material mainly consisting of CEC. Upon heating, the solubility in CEC increases. This accounts for the slow melting process of the crystalline leaflets which extends over a temperature range of nearly 100° depending on the heating rate. These observations disprove Durand and Lee's[4] assignment that the leaflets are ordinary crystallites of CEC.

Experimental Measurements

The optical rotatory power (OR) was used as a probe for the determination of the sense of the cholesteric helical structure. It was measured polarimetrically at a wavelength of 5893 Å as previously described.[8] The sample was sandwiched between quartz discs held apart by a 10μ mylar spacer. In order to determine the dispersion curve of OR, the rotation angle was measured with a polarizing microscope, using interference filters to select certain wavelength bands in the range 4000 to 7000 Å. The texture of the cholesteric phases and the transition

- 3 -

temperatures were checked microscopically.

Results and Discussions

Pure CEC has a reversible cholesteric-isotropic transition temperature $T_{is \to chol}$ = 31.0 ± 0.5°. Upon slowly cooling, solidification occurs at 15°. However, if the sample is allowed to stand at room temperature for a few days $T_{chol \to s}$ = 24.5°. The solid-cholesteric transition temperature is $T_{s \to chol}$ = 24.5°. The values are in disagreement with Durand's data.[2] The isotropic and cholesteric phases are homogeneous with no evidence for partial crystallization. The cholesteric phase shows positive optical rotation (Fig. 2, curve 1) and the data are well reproducible on heating and cooling. For $T > T_{is \to chol}$ and $T < T_{chol \to s}$ the OR vanishes abruptly. Clearly no change in sign of the OR occurs which could indicate a change in the sense of the helix.

The correlation between the sense of the helical screw and the sign of the resulting OR is given by de Vries' formula:[9]

$$r = 360/8Z \cdot \alpha^2/\lambda'^2(1-\lambda'^2) \qquad (1)$$

r is the specific rotation in deg cm^{-1}. Z is the pitch of the helix, $\alpha = \Delta n/\bar{n}$ is the relative birefringence of the layers constituting the cholesteric structure, $\bar{n}$ is the mean refractive index and $\lambda' = \lambda/\bar{n}Z$ where λ is the wavelength of the analyzing light. $\bar{n}Z$ is the wavelength of maximum reflection. The definition of the sign is such that a right handed helix, defined by $Z > 0$ rotates the plane of plane polarized light moving towards an observer clockwise ($r > 0$). Two limiting cases have to be considered:

$$r = 360Z/8\lambda^2 \cdot \alpha^2 \bar{n}^2 \quad \text{for } \lambda \ll \bar{n}Z \qquad (2)$$

$$\text{and} \qquad r = -360/8\lambda^4 \cdot Z^3 \bar{n}^4 \alpha^2 \quad \text{for } \lambda \gg \bar{n}Z \qquad (3)$$

In order to determine the sign of Z from the sign of r, it is there-
fore necessary to know whether one is on the short or long wavelength
side of the reflection band. For that purpose the dispersion curve of
OR in pure CEC displaying the plane texture was measured (see Table I).
The experimental data can be fitted to eq. 1 if one makes the following
choice for the parameter values: $\lambda_o = \bar{n}Z = 9000$ Å and $\alpha = 3.07 \times 10^{-2}$.

Table I

Experimental and Calculated Value for the Rotation Angle of a 25.4μ CEC

Sample at Room Temperature

λ [Å]	ϕ_{exp} (deg) error ±0.5°	ϕ_{calc} (deg)
4000	12.0	11.5
4330	10.0	10.3
4660	9.0	9.1
5000	8.0	8.4
5330	7.5	7.9
5660	7.5	7.5
6000	7.0	7.1
6330	7.0	7.2
6660	7.5	7.3
7000	7.5	7.4

The value for λ_o was confirmed by a measurement of the distance of neighboring Grandjean lines in a wedge-type sample[10,11] which provides a direct determination of the pitch. The result was $Z = 6000 \pm 300$ Å at room temperature yielding $\lambda_o = 9000 \pm 500$ Å by using the experimental value $\bar{n} = 1.503$ for the mean refractive index. These results show that pure CEC forms a right handed cholesteric structure which does not undergo helical inversion.

In order to probe the influence of impurities on the results obtained with commercial CEC, two samples of unpurified CEC were examined. Both were taken from material stored in a bottle which had been allowed to stand for 4 months. Because the specific weight of the crystallites present in commercial CEC is slightly higher than that of the bulk material, they are subject to sedimentation. A sample (referred to as No. 2) prepared from material from the top of the bottle therefore contained only very few crystalline leaflets. Its behavior was similar to that of pure CEC. The optical rotation of the cholesteric phase is positive (Fig. 2, curve 2), the helix right handed. The transition temperatures, however, are shifted to lower values $(T_{is \to chol} = 22.5°)$ indicating the presence of some impurities.

A completely different behavior is observed with a sample (No. 3) prepared from the thoroughly stirred contents of the bottle. At room temperature roughly half of the sample consists of crystallites randomly distributed in the isotropic bulk material showing practically no OR. After melting the crystallites at higher temperatures and recooling, a homogeneous phase is formed which becomes cholesteric at

$T_{is \to c}$ = 37.5° and can be supercooled to -60° without solidification (observation time 2 hours). The optical rotation measured at the short wavelength side of the reflection band is negative indicating a left-handed cholesteric structure. The pitch must be of the order of 1μ. This suggests that dicholesteryl carbonate (DC), which is the most likely crystallite impurity, tends to form a left-handed and tightly wound cholesteric structure.[12] Mixing two compounds one of which is capable of forming a right-handed and the other a left-handed structure can produce helical compensation as has been shown by a number of investigations.[3,8,13] If, for example, the relative concentration of the "right handed" species has a critical value C_{ro}, the resulting structure is nematic. For $C_r > C_{ro}$ a right-handed and for $C_r < C_{ro}$ a left-handed cholesteric phase is formed. In the "well stirred" sample of CEC obviously the concentration of CEC was below its critical value, so that DC dominated helix formation. Upon lowering the DC-concentration, one must pass through a mixing ratio at which the nematic phase exists at a temperature which is within the mesomorphic range. Durand[2] must have observed this phenomena.

It therefore appears that no single component material is known which displays a thermally induced helical inversion, and that impurities can play an important role in the properties of liquid crystalline systems.

Correlation Between Molecular Optical Activity and Helical Sense

Dissolution of an optically active cholesteryl ester in the nematic phase of p-azoxyanisole or p-azoxyphenetole[14] leads to the

- 7 -

formation of a cholesteric mesophase with a pitch inversely proportional
to the solute concentration. This result, and the fact that all choles-
teric mesophases which are known so far are composed of optically
active compounds, led to the conclusion that optical activity is a
necessary condition for the twisted cholesteric structure becoming
energetically stable. In addition, there is some support for the
assumption that the sense of the helical screw is identical with the
sign of the optical rotatory power of the constituting molecules: (1) a
racemic mixture of p,p'-diactive amyloxyazoxybenzene mixed with p,p'-
di-n-hexyloxyazoxybenzene does not form a cholesteric phase but the
optically active compound does;[15] (2) dextro-rotatory amyl p-(4-cyano-
benzylideneamino)cinnamate forms a right handed helix, laevo-rotatory
cholesteryl benzoate a left-handed helix and a mixture of both gives
a compensated structure at an appropriate mixing ratio.[13] .The present
investigations, however, show that the sense of the helical screw and
of the specific optical rotation do not always agree (see Table II).
Both pure CEC and cholesteryl chloride are laevo-rotatory on a molecular
basis but form a right handed helix. Both compounds can be mixed with
a laevo-rotatory compound, which alone produces a left handed helix, to
form a compensated structure. In particular, a 1.75:1.00 weight mixture
of cholesteryl chloride and cholesteryl myristate is not racemic. It
gives rise, however, to a compensated helical structure. With molecules
containing more than one asymmetric carbon site, the relationship between
molecular optical activity and the helical sense which they can establish
either as a pure mesophase or as solutes in a nematic phase is therefore

- 8 -

rather complex. Further investigations of the nature of this relation-
ship are in progress.

Table II

Comparison Between Specific Optical Rotation (Measured in Chloroform
Solution at Room Temperature) and Sense of the Helix

Compound	Specific Optical Rotation α_D	Helix Sense
cholesteryl 2-(2 ethoxyethoxy)		
ethyl carbonate (CEC)	-22.0	right-handed
dicholesteryl carbonate (DC)	<0	left-handed[12]
cholesteryl chloride (C)	-30.8[14]	right-handed[13]
cholesteryl myristate (M)	-26.5	left-handed[13]
C:M = 1.75:1.00	-28.8	compensated at
		T = 42°

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Figure Captions

Figure 1: Infrared Spectra of CEC Samples in the Carbonyl and C-O
Vibration Region. (A) Pure CEC; (B) Major Impurity;
(C) Commercial CEC.

Figure 2: Specific Optical Rotation as a Function of Temperature of
CEC Samples. Curve 1, Pure CEC; Curve 2, Commercial CEC
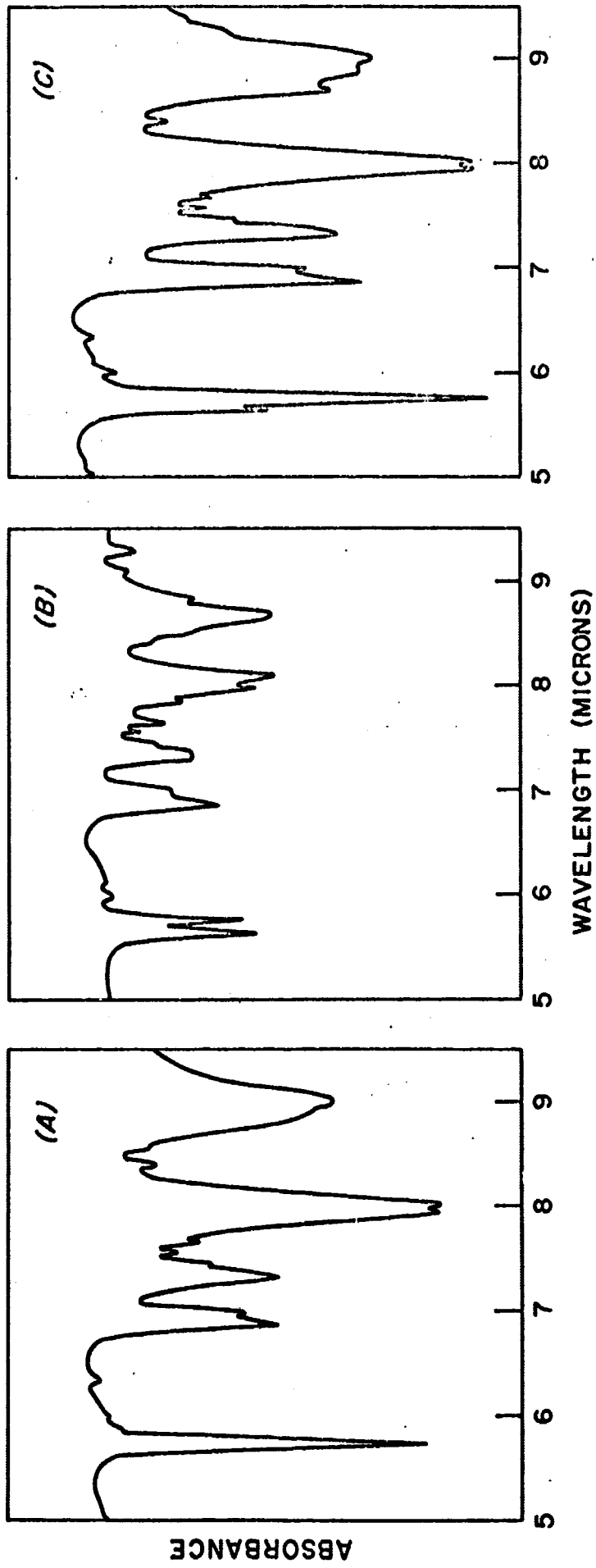from which crystallite impurity has sedimented; Curve 3, well-
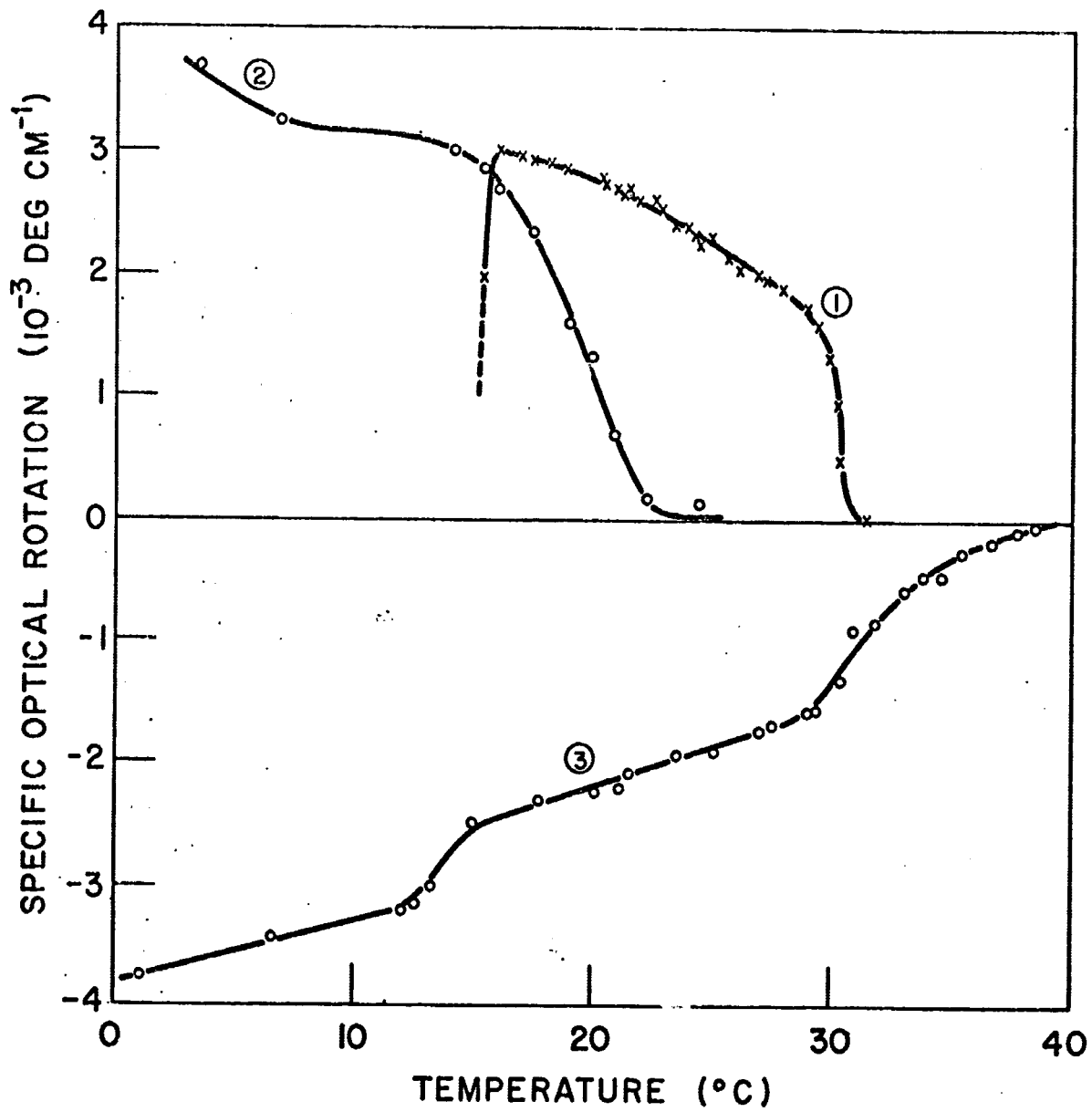stirred commercial CEC.

Figure 1

WAVELENGTH (MICRONS)

ABSORBANCE

Figure 2

Helical Twisting Power of Steroidal Solutes in Cholesteric Mesophases

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Shifts in the nematic temperature of a compensated cholesteric liquid crystal solvent, consisting of cholesteryl chloride and cholesteryl myristate, are caused by adding steroidal solutes. A helical twisting power P can be defined which is a molecular property; there is a linear dependence of the inverse on the solute concentration of the helical pitch. The method has the advantages of (1) allowing study of compounds which do not form mesophases themselves and (2) eliminating temperature effects. For a series of fatty acid esters of cholesterol, P decreases with decreasing number of carbon atoms in the ester chain, and shows a zigzag fine structure with P having higher values for odd-numbered carbon atom chains. P, and therefore the helix, changes rotational senses if the ester chain is replaced by Cl, Br, or OH. Changes are also discussed associated with modifications of the 17 side chain or the steroid ring system itself. A model is proposed attributing P to the molecular asymmetry at the 3β position of the steroid ring, which can cause macroscopic twist if two lever arms are present, one of which lacks rotational symmetry.

Introduction

In cholesteric liquid crystals, the molecules form a layer-like structure, each layer representing a two-dimensional nematic liquid crystal, but subsequent layers being twisted by a small angle. Some unusual optical effects[1,2] originate from this resultant helical structure. The conditions which must be fulfilled in terms of molecular properties in order to stabilize such a twisted structure energetically are not well understood.[3] Since all cholesteric liquid crystals consist of optically active molecules, it has been suggested that such molecules possess a built-in structural screw sense which can manifest itself in the formation of a helical structure provided that other critical structural requirements such as the rodlike molecular shape are fulfilled. However, such a correlation between optical activity and helix formation, if it exists, cannot be a simple one, since it has been found[4] that the rotational sense associated with both phenomena does not always coincide. Furthermore, Fergason, Goldberg and Nadalin[5] have shown that the near planarity of the steroid ring system is of crucial importance.

In order to further elucidate the stereochemical requirements for the formation of cholesteric mesophases, experiments were carried out to determine the additional structural twist which is introduced into a compensated cholesteric liquid crystal by adding other rodlike molecules. This method provides two important

- 1 -

advantages: (1) it enables investigation of compounds which do not form a mesophase themselves, but which are similar in shape to the solvent molecules, leaving the solvent essentially undisturbed; (2) it allows comparison of the influence of different solute molecules in a constant molecular environment at a given temperature. The solute molecules chosen for the present investigation include a series of fatty acid esters of cholesterol, cholesterol, cholestanol, cholesteryl halides, and compounds containing variations in the side chain system attached to the C17 position of the steroid ring. The matrix was a compensated cholesteric liquid crystal consisting of a mixture of cholesteryl chloride and myristate,[6,7] adjusted to give a nematic phase at a temperature between 30 and 40°.

Description of the Method

The principal parameter characterizing the cholesteric structure is the pitch Z of the helix; Z^{-1} is proportional to the twist angle between subsequent layers of the cholesteric structure, and can also be regarded as the wavenumber of the helical structure. Measurement of a change in twist - either thermally induced or caused by addition of solute molecules - is therefore equivalent to measuring changes in the pitch. A convenient way to do this is to record the optical rotation (OR) of the helical structure. The sample must be prepared so that it displays a plane texture, i.e. the helix axis must be parallel to the light direction. In the

- 2 -

present case Z is always much greater than λ_o, the wavelength of

the analyzing light (λ_o = 5893 Å). Therefore, the following

approximation of de Vries'[1] equation connecting OR and pitch can

be employed:

$$r = (360/8\lambda_o^2)Z(\Delta n)^2 \qquad (1)$$

i.e. $$Z^{-1} = \text{const} \times r^{-1} \qquad (2)$$

r is the specific optical rotation in deg cm^{-1} and Δn is the

anisotropy of the refractive index of the layers constituting the

helical structure. Δn can be temperature dependent. In order to

derive absolute values for Z from OR measurements, it is necessary

either to measure Δn or to calibrate eq. 2 using a method which

yields Z directly.[7] Such techniques are: (1) recording the

diffraction pattern of the cholesteric structure;[6] (2) optical

transmittance measurements near $_r$ = nZ, n being the mean refractive

index;[8] (3) determination of the distance of Grandjean lines in a

wedge type sample.[9] For the interpretation of the present results,

the value for the constant in eq. 2 was derived both from literature

data[6] for Z(T) and from IR transmittance data in the temperature range

20 to 60°.[8]

The optical rotation was determined with a Rudolph polari-

meter. Details are described elsewhere.[7] The sample was sandwiched

- 3 -

between polished quartz discs which were kept at a distance of 10μ by a mylar spacer. The sample texture was checked with a polarizing microscope.

Cholesteryl chloride (C) and cholesteryl myristate (M) were obtained from Steraloids Inc. In order to have identical mixtures of both compounds as a solvent for a series of runs two batches were prepared using a ballmill for thorough mixing. A 190:100 weight mixture of C:M yielded a cholesteric structure which was exactly compensated at T_{nem} = 32.5°, a 175:100 C:M mixture gave T_{nem} = 39.8°.[10] T_{nem} is reproducible within ±0.3° for different samples of the same batch. In the following discussion, these mixtures will be referred to as CM190 and CM175. A homologuous series of cholesteryl esters (I), cholesterol and cholestanol (II) to use as solutes were obtained from Steraloids or Aldrich. Δ^5 dehydroepiandrostene-17 one-3β myristate (dehydroepiandrosterone myristate)(III), $\Delta^{5,24(28)}$ cholestene-3β-myristate (fucosteryl-myristate)(IV) were synthesized from the appropriate sterol by esterification with myristoyl chloride in pyridine.

$C_{n-1}H_{2n-1}COO$ I

HO   II

$C_{13}H_{27}COO$ III

$C_{13}H_{27}COO$ IV

- 4 -
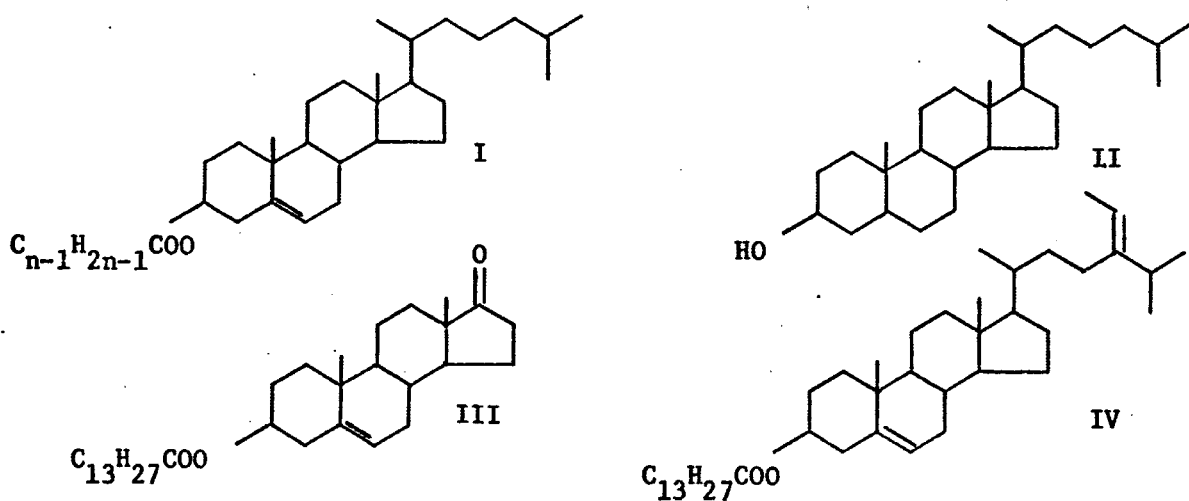
The idea of inferring a molecular twisting power, P, of

a molecule from its influence on the pitch of a compensated choles-

teric phase is based on an observation made by Cano and Chatelain.[11]

They found that upon adding cholesteryl benzoate, which itself can

form a cholesteric phase, to nematic p-azoxyphenetole, a cholesteric

structure is produced with a pitch inversely proportional to the

concentration of the solute. The following results show that this

finding also applies to a cholesteric matrix.

Fig. 1 shows the temperature dependence of the helix wave

number Z^{-1} on temperature for CM190 at different relative molar

concentration c of excess cholesteryl myristate. With increasing c

the curves $Z^{-1}(c)$ experience a parallel shift to higher temperatures.

Their intersection with the abscissa yields $T_{nem}(c)$, with $T_{nem}(c)$

being a linear function of c (Fig. 2). This means that the family

of curves of Fig. 1 can be described by

$$Z^{-1}(T) = m(\Delta T - \Delta T_{nem}(c)) = m(\Delta T - c\Delta T_{nem}^{(s,o)}) \qquad (3)$$

Here m is the slope of the curves in Fig. 1, its numerical value

being 250 ± 10 $(°C \times cm)^{-1}$, $\Delta T = T - T_{nem}$, where T_{nem} is the nematic

temperature of the matrix. $c\Delta T_{nem}^{(s,o)} = \Delta T_{nem}(c) = T_{nem}(c) - T_{nem}$

is the shift in the nematic temperature which is produced by a solute

s of concentration c. $m\Delta T = Z_o^{-1}(T)$ is the helix wavenumber of the

cholesteric matrix at a temperature T. The change in wavenumber

- 5 -

which is caused by the solute is therefore given by

$$z^{-1} - z_o^{-1} = z_s^{-1}(c) = -mc\Delta T_{nem}^{(s,o)} = -m\Delta T_{nem}(c) \qquad (4)$$

Several conclusions can be drawn from eq. 4: (1) z_s^{-1} is independent of temperature. This allows the study of the molecular twisting power of various solutes independent of temperature by measuring $\Delta T_{nem}(c)$; (2) a helical structure represents a special case of a standing circular polarized wave. A negative sign of $z_s^{-1}(c)$ means that the solute molecules introduce additional left-handed twist, a positive sign means right-handed twist. A net left-handed helical twist causes laevo-rotation in OR measurements (r < o in eq. 1) (3). The existence of a linear relationship between $z_s^{-1}(c)$ and c means that - at least in the investigated concentration range[12] - an additivity law for helical twist is valid. One can therefore extrapolate to c = 1 in order to obtain $z_{s,o}^{-1} = z^{-1}(c)/c$. This quantity is a measure of the molecular twisting power P of the solute molecules. If the solute can form a cholesteric phase itself, $z_{s,o}$ should be approximately equal to its pitch.

Results

The method described above of inferring the specific helical twist which solute molecules can exert on an ordered cholesteric structure was applied to a homologuous series of fatty acid esters of cholesterol and some related compounds. Most experiments were

- 6 -

performed at a relative molar concentration of c = 0.055, which

leaves the matrix structure essentially unchanged, as evidenced

by the absence of a significant change in the isotropic-cholesteric

transition temperature. Fig. 3 shows the dependence of ΔT_{nem}

(c = 0.055) on the number of carbon atoms(n) in the ester chain.

All cholesteryl esters introduce a left-handed helical twist to

the liquid crystalline matrix, which goes to zero as n approaches 1.

Fig. 4 shows that the decrease in twisting power with decreasing n

is not accompanied by a decrease in the specific molar optical

rotatory power of the esters. On the contrary, the experimental

values for α_m, which agree with literature data,[13] display only a

minor dependence on n. This is to be expected, since the ester

group is optically inactive and does not perturb conformation within

the steroid ring system significantly.

In order to explore the influence of the C17 chain in the

steroid ring system on the molecular twisting power, two compounds

were examined: dehydroepiandrosterone myristate, which has only a

carbonyl group at the C17 position and fucosteryl myristate which

has an additional ethylidene group at the C24 position. Both pure

compounds do not themselves form a mesophase, a result which is

particularly noteworthy in the case of fucosteryl myristate. In

solution, however, ΔT_{nem} and therefore the twisting power, is only

about 20 per cent less than that of cholesteryl myristate(Fig. 3). This

indicates that: (1) the steroid side chain is not of major signifi-

cance to the molecular twisting power P and that (2) apart from P

- 7 -

a structurally sensitive factor plays a crucial role in the ability

of molecules to form a cholesteric phase.

These results suggest that the group occupying the 3β -position

of the steroid ring is the functional group mainly responsible for

the molecular twisting power. This is further illustrated by the data

listed in Table I. If the ester group is replaced by a halogen atom

or a hydroxyl group, the helical twist changes sign from left-handed

to right-handed ($\Delta T_{nem} < 0$), and P is almost independent of the nature

of the group. It also remains unchanged if the double bond in the

cholesteryl ring is saturated or if the steroid side chain at C17

is replaced by a keto-group. Again, no correlation between the

sense of the helical twist and the sign of the molecular optical

activity exists.[4]

Discussion

A. Relationship Between Molecular Structure and Helical Twist

For the sake of simplicity let us assume that the molecules

constituting a cholesteric phase resemble a rod with the long axis

perpendicular to the helix axis (although this is not always exactly

true[14]). One condition for the macroscopic structural twist to

occur, however, is that the molecules display some deviation from

an ideal rotational ellipsoidal shape. They must contain an asymmetric

center, i.e. the molecules must not be superimposable on their

mirror image by translation or rotation. Otherwise no distinction

between a right-handed and a left-handed helical screw is possible.

This is the identical condition for optical activity of individual molecules. There is, however, an essential difference: the optical activity caused by an asymmetric carbon atom in a molecule is determined by the mutual directions and the magnitudes of the electric and magnetic optical transition moments, which are given by the wave functions of ground and excited states. This implies that the cross section for interaction between a photon and the asymmetric carbon atom cannot be larger than the atomic cross-section. This is not true in the case of structural twist, because in order to become effective in producing an asymmetric molecular arrangement, an asymmetric center must produce or must be subject to anisotropic intermolecular forces. In the compounds under consideration, forces between induced dipoles give the major contribution to the cohesive energy. This implies that forces acting between groups of neighboring molecules depend on the electronic polarizability and hence on the number of electrons bound within the group. Therefore an asymmetric carbon atom can only produce structural twist if sufficiently long lever arms are attached to it causing anisotropy of the polarizability. This makes it energetically favorable for lever arms of the asymmetric centers of neighboring molecules to arrange themselves in a parallel array. Qualitatively this can explain that (1) the molecular twisting power of cholesteryl esters increases with the length of the ester chain and that (2) a steroid ring system containing several asymmetric centers without lever arms

- 9 -

is unimportant in producing twist.

Nevertheless, the presence of the steroid ring system is necessary to define the rotational sense of the molecular screw. This can be seen from the following model. Fig. 5a shows the structure of cholesteryl nonanoate (n=9). The steroid ring system defines a central molecular plane. From steric reasons it is very likely that the position of the carbonyl group is as indicated, i.e. approximately parallel to this plane. The conformation in the 3β position is such that the C 3 -O bonds makes an angle of the order of 5° with the plane, pointing out of the plane towards an observer. This means that the ester chain makes an angle of approximately 5° with the central molecular plane and its projection into the plane forms an angle $\stackrel{\sim}{\sim}$ 10° with the long axis of the steroid ring system. Thus, the molecule behaves as part of a left-handed screw, the C3 atom representing the active asymmetric center. Considering that rodlike molecules tend to arrange themselves with their long axes parallel, and that the resulting structure is apolar,[15] four possibilities can be envisaged for the position of a second molecule with respect to a first one (Fig. 5b). Translational motion does not cause principal changes. Molecular rotation around a long axis is restricted insofar as the energetically stable configuration will probably be one with parallel central molecular planes. Fig. 5b shows that arrangements 1, 2 correspond to a left-handed structural twist and arrangements 3,4 are "neutral". Clearly the twist can only become macroscopically effective if the molecules are subject

- 10 -

to forces producing long-range order. Thus, the inherent molecular

screw sense must produce left-handed helical twist, both if the

molecules are imbedded in a nematic or cholesteric solvent phase

or if they form a liquid crystalline phase themselves. The twisting

power is a molecular property. This explains why an additivity

law holds over a wide range of concentration.

A tetragonal asymmetric carbon center which is not connected

to a ring defining a molecular plane cannot produce helical twist as

can easily be seen from the following argument. Since only rod-like

molecules are compatible with liquid crystalline long range order,

the asymmetric carbon atom should not contain more than two lever

arms. However, if both lever arms consist of linear chains, rotational

motion around these chains prevents formation of a macroscopic screw.

This point was experimentally verified by the observation that neither

d- nor l- mandelic acid $[C_6H_5CH(OH)CO_2H]$ cause a shift in the nematic

temperature of the CM mixture. This explains why the cholesteric

liquid crystalline structure is found with derivatives of cholesterol

and cholestanol:[5] the steroid ring system serves (1) as a second

lever arm acting at the C 3 position and (2) as a plane to define

a molecular screw sense. Cholesteric phases can also be formed by

optically active acids and alcohols if they contain aromatic rings

establishing a molecular reference plane. This has recently been

verified by Leclercq, Billard and Jacques[16] in the case of alkoxy-

biphenylcarboxylic acids and arylidene-p-aminocinnamic acid esterified

with an optically active alcohol.

The relative unimportance of the steroid side chain at the C 17 position can also be understood on the basis of the present model: some rotational freedom around the C 17 - C 20 bond makes it possible for the chain axis to be parallel to the central plane, so that the chain cannot contribute to asymmetry. It is therefore reasonable that removal of this chain causes only a slight reduction of the molecular twisting power. However, this side chain is important in the establishment of the cholesteric structure in pure compounds as will be discussed below.

Further confirmation for the model presented herein is based on the observation that the structural twist produced by derivatives of cholesterol changes sign if the fatty acid group is replaced by a halogen or a hydroxyl group. Fig. 5a shows that the projection of the bond vector at the 3β position in the molecular plane is rotated anticlockwise with respect to the long axis of the steroid ring system giving rise to a right-ha ed molecular screw. Therefore the sense of the molecular twist' power must change sign when going from an ester with n > 1 n = 0. In the methyl ether of cholesterol, the ether group has a center of mass located near the long axis of the cholesteryl group. This compound has a negligible twisting power (see Fig. 3).

B. Dependence of the Helical Twist on the Ester Chain Length

In the curve ΔT_{nem} ∿ P = f(n) (Fig. 3) a fine structure is observed which is outside the experimental error. For n < 9 the experimental values ΔT_{nem} fit a zigzag curve, the lower values being

observed for an even number n of carbon atoms. Similar curves have been obtained for the transition temperatures.[17] The explanation for this behavior is evident from the structural model (Fig. 5b): the distance between the end of the ester chain and the extrapolated long molecular axis of the steroid ring system is a measure of molecular asymmetry and hence of the molecular twisting power P. This distance varies in a zigzag fashion from even to odd C atom chains. In the appendix an explanation for the functional dependence of P on the ester chain length is presented.

C. Calculation of the Helix Pitch

Measurement of $\Delta T_{nem}(c)$ at a given concentration allows calculation of the wavenumber $Z_s^{-1}(c)$ of the cholesteric structure produced by the concentration c of asymmetric solute molecules in a liquid crystalline matrix. Extrapolation to c = 1 yields a value for the reciprocal pitch $Z_{s,o}^{-1}$ of the cholesteric phase of the pure solute. In the cases where this cholesteric phase does not exist this value only represents a number which can be used to characterize the twisting power of the molecules. Table II gives values derived from the present measurements.

The agreement between the pitch values calculated from $Z_s^{-1}(c)$ and the few literature values available is fairly good (Table II) illustrating the validity of the additivity law. It is particularly noteworthy that the value for cholesteryl chloride is identical with the one derived from the concentration dependence of Z in a mixture of C and p-azoxyanisole.[18] This shows that the twisting power is indeed a molecular property independent from the

- 13 -

matrix.

The fact that there are a number of compounds which are sufficiently asymmetric to show molecular twisting power characterized by $Z_s^{-1} \neq 0$ but that do not form a mesophase themselves indicates that, aside from asymmetry, there must be further criterion for the stability of the cholesteric phase. It is clear from the present study, as well as the literature that structure in the 3- position, the steroid ring system and the 17- side chain are all of critical importance to the existence of a mesophase in a pure compound.

Concluding Remarks

Recently an interesting dynamic theory for the cholesteric phase was published by Keating.[20] He shows that thermally excited molecular rotations around a short molecular axis parallel to the helix axis can lead to a non-varishing time average of the rotation angle, and hence to a twist between neighboring cholesteric layers provided that the forces opposing rotation are anharmonic. Thus helical twist has its origin in a physical process similar to thermal expansion. The theory predicts that $Z^{-1} \sim T/I$ in a temperature range sufficiently apart from a transition temperature, I denoting the molecular moment of inertia. Experimentally the present as well as previous[8] results confirm the above relationship excellently. Furthermore, the model is able to predict helical inversion in a cholesteryl chloride - cholesteryl myristate mixture of appropriate

- 14 -

mixing ratio. Because C molecules are shorter than M molecules the moments of inertia for rotation around a short axis fulfill the inequality $I_C < I_M$ thus causing a faster decrease of Z_C^{-1} with decreasing temperature than of Z_M^{-1}. Since $Z_{CM}^{-1} = c_C Z_C^{-1} + c_M Z_M^{-1}$ helical inversion has to be expected.

The connection between Keating's dynamical approach and the static model presented herewith is given by the intermolecular forces. The repulsive forces are sufficiently asymmetric only if the molecules are asymmetric in the described way. In this respect it is, however, surprising that one can define a molecular twisting power which is virtually independent of the liquid crystalline matrix.

Appendix

Neglecting the zigzag structure of the ester chain the distance a between the end of the chain and the extrapolation of the long axis of the steroid ring system can be expressed by

$$a = nb \sin\alpha - \delta a \qquad (1)$$

b is the projection of the C-C-bond length on the chain axis. δa accounts for bending of the chain caused by intermolecular forces which tend to make the chain axis parallel to the axis of the ring system. δa can be calculated from the expression for the bending of a thin rod under the influence of a constant force K acting per unit length perpendicular to the rod axis: $\delta a \sim dx \cdot dK \sim (dx)^2$. Integration yields

$$a \sim P \sim nb \sin\alpha - const \times (nb)^2 \qquad (2)$$

Since $P \sim \Delta T_{nem}$, eq. 2 can be checked by plotting the difference between the extrapolated curve $\Delta T_{nem} \sim n$ and the averaged experimental curve (see Fig. 3) versus n. The result is a curve rising $\sim n^2$ as predicted by eq. 2. Slight deviations occur for n > 10 indicating that P approaches a saturation value for large values of n.

Table I

Shift in the Nematic Temperature Caused by Compounds Giving

Positive Twist

Compound	ΔT_{nem} (c=0.055)(°C)
Cholesterol	-4.8
Dehydroepiandrosterone	-4.5
Cholestanol	-5.0
Cholesteryl chloride	-7.0
Cholesteryl bromide	-6.0

Table II

Calculated and Experimental Pitch Values

Compound	Number of C-atoms in the ester chain	Z_{calc} (Å)	Z_{exp} (Å)
Cholesterol	0	4900	
Dehydroepiandrosterone	0	5200	no
Cholesteryl formate	1	15000	liquid
Cholesteryl acetate	2	8400	crystals
Cholesteryl proprionate	3	3100	3000[10]
Cholesteryl butyrate	4	2900	
Cholesteryl valerate	5	2200	2600[10]
Cholesteryl caproate	6	2120	
Cholesteryl pelargonate	9	1720	2400[10]
Cholesteryl myristate	14	1340	
Cholesteryl palmitate	16	1300	
Cholesteryl chloride		3380	3400[18]

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Figure Captions

1. Temperature dependence of the helix wavenumber Z^{-1} of CM 190 at various relative molar concentrations of excess cholesteryl myristate. Δ: Values obtained from infrared - absorption measurements. x: CM 190 doped with $c = 0.055$ cholesteryl caproate ($n = 6$).

2. Dependence of the nematic temperature T_{nem} of CM 190 on the relative molar concentration of excess cholesteryl myristate.

3. Dependence of the shift in the nematic temperature of CM 190 and CM 175 on the length of the side chain attached to the 3β position of various solute molecules ($c = 0.055$).

     o   :   esters between fatty acids and cholesterol

     □   : dehydroepiandrosterone myristate

     ▣   :   fucosteryl myristate

     ▲   :   dehydroepiandrosterone

     ●   :   cholesterol

     ✗   :   cholestanol

     +   :   cholesteryl-methylether

4. Molar optical rotatory power of cholesteryl esters as a function of the number of carbon atoms in the ester chain.

5. (a) Structure of cholesteryl nonanoate, α denotes the angle between the extrapolated long molecular axis of the steroid ring system and the axis of the ester chain. The ester chain points towards the observer.

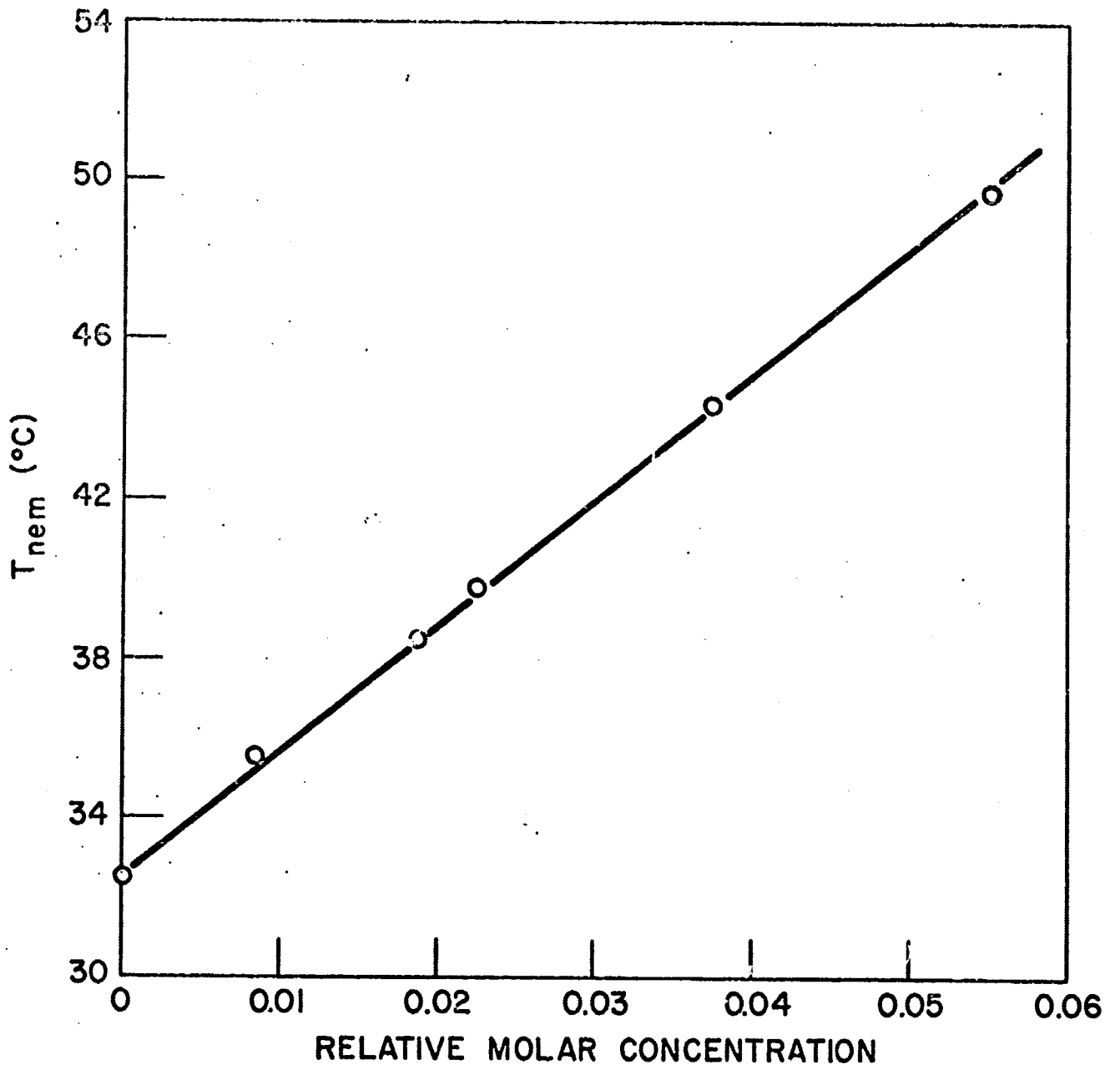   (b) Possibilities for the mutual arrangement of two cholesteryl ester molecules.
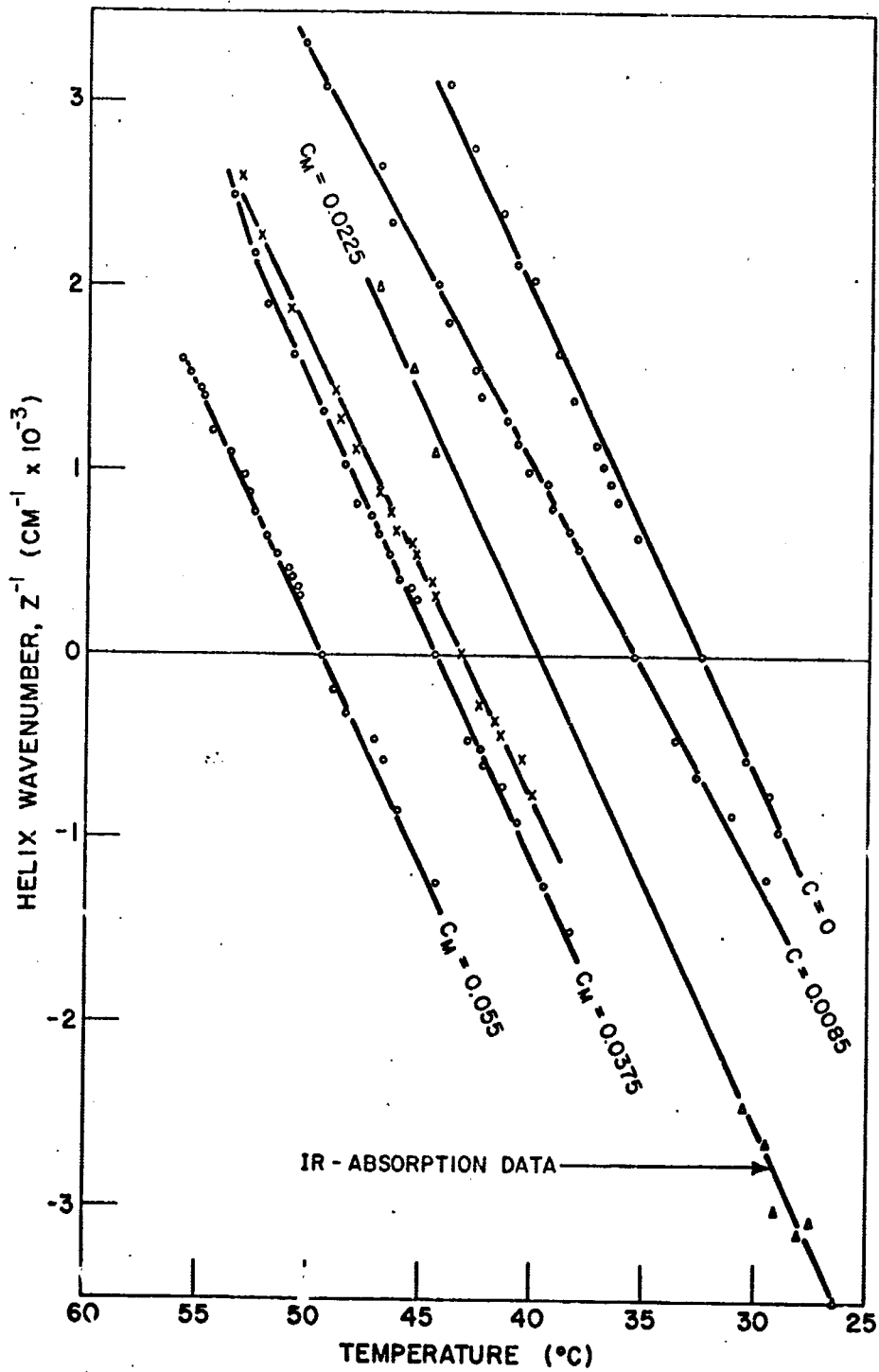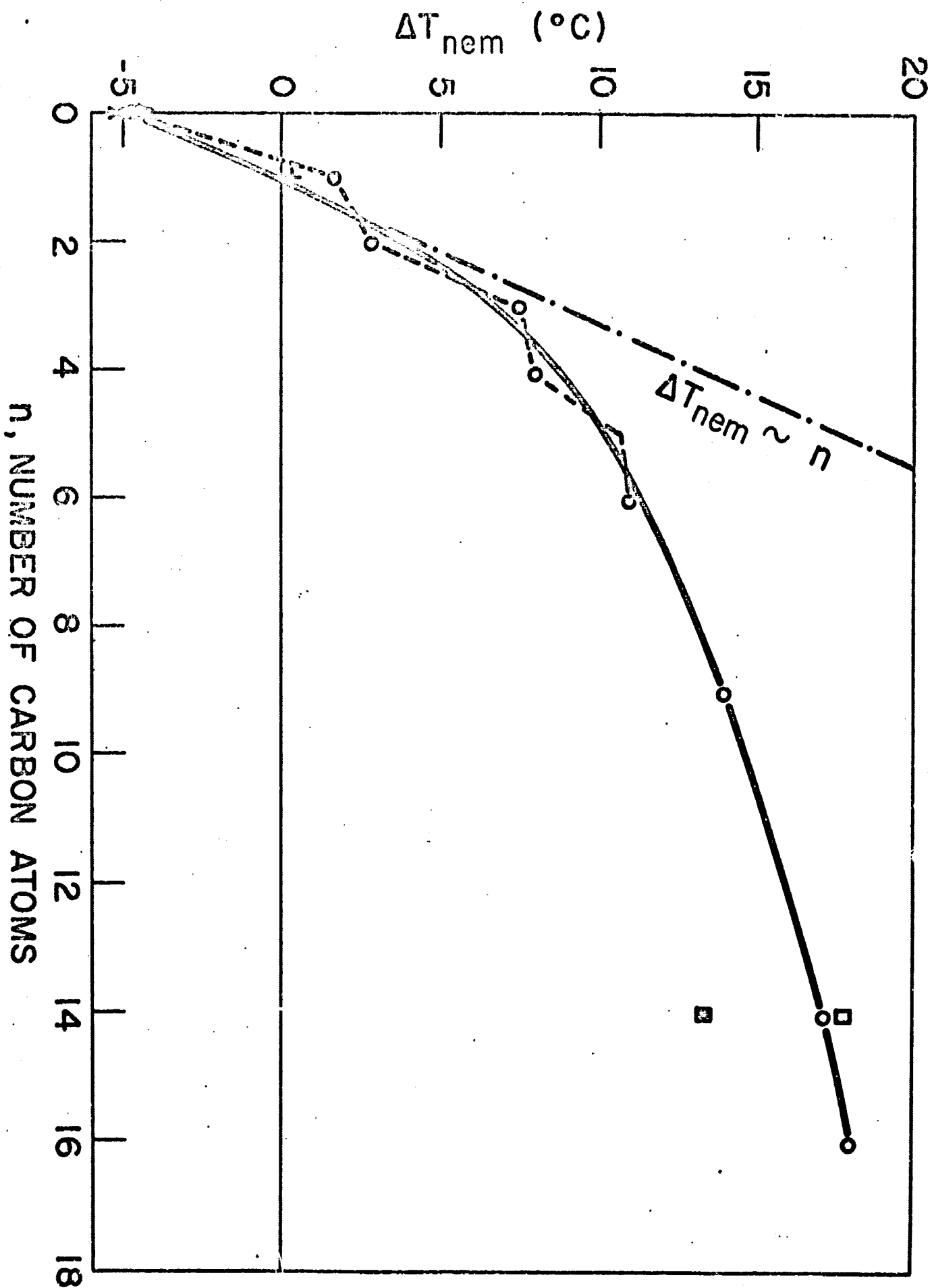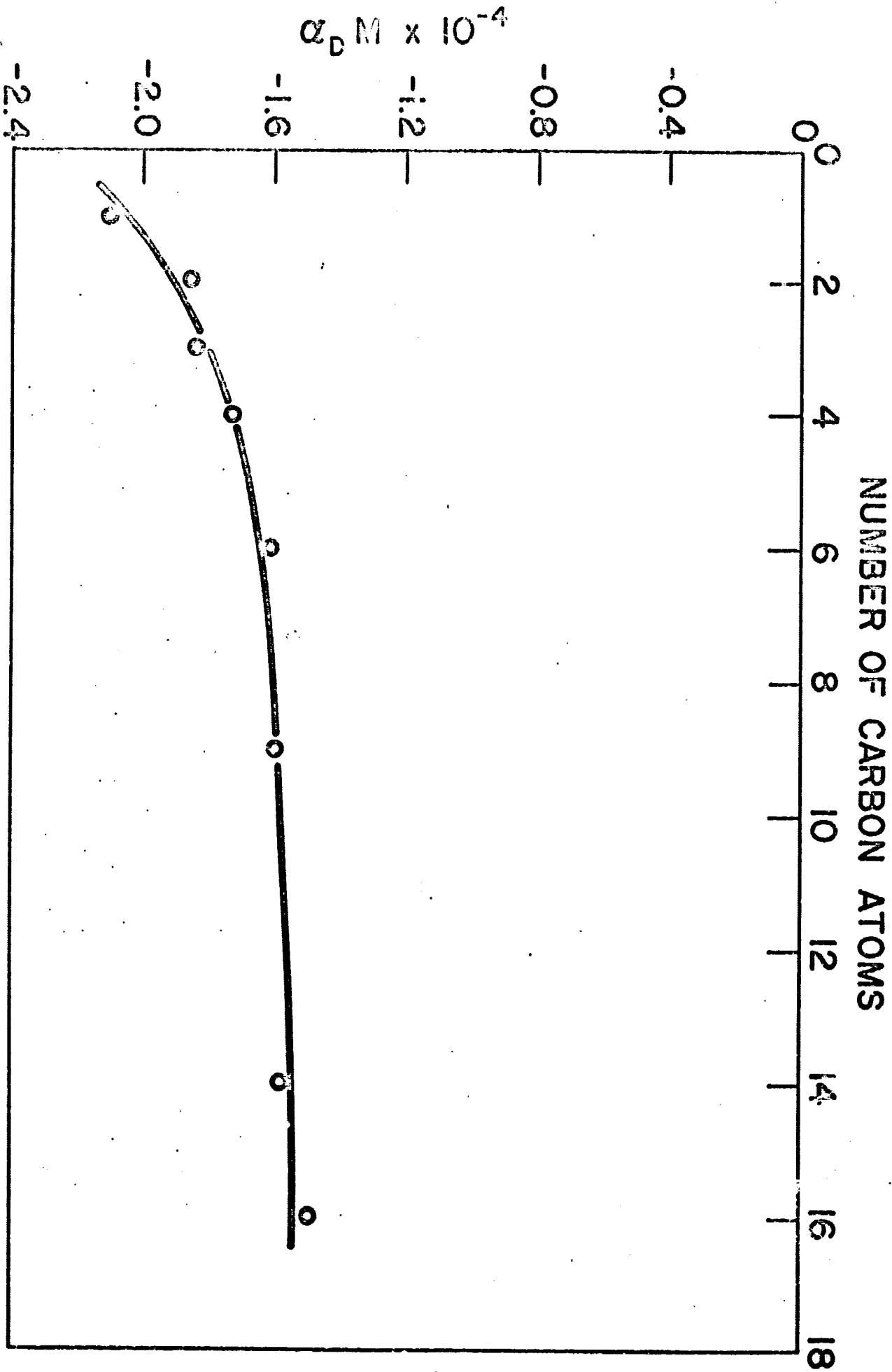
Figure 1
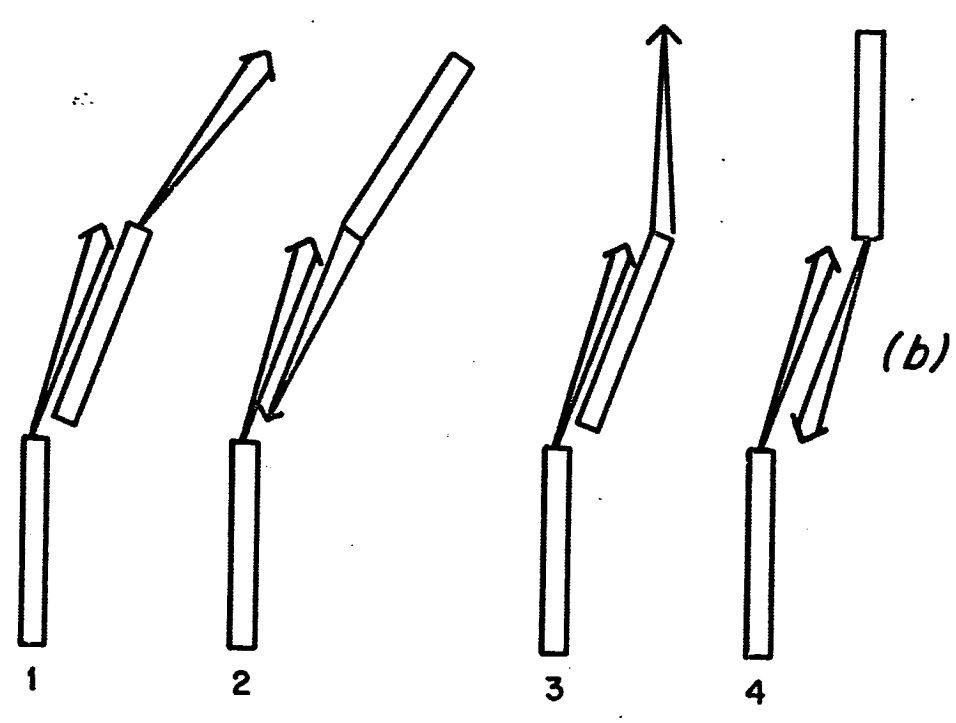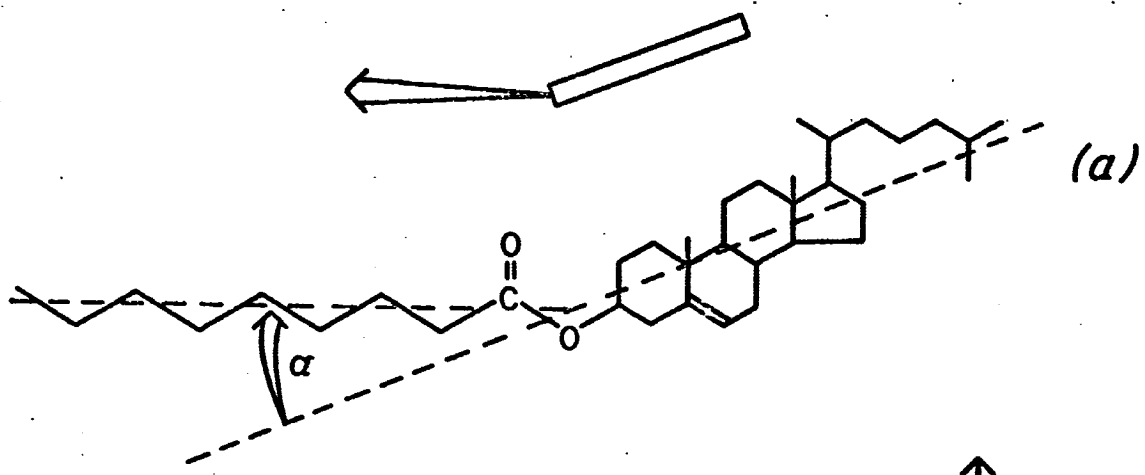
Figure 2

Figure 3

Figure 4

Figure 5

Determination of the Pitch of a Cholesteric Liquid Crystal by

Infrared Transmission Measurements[*]

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The pitch of a cholesteric liquid crystal can be inferred

from (1) the distance of the Grandjean lines in a wedge type sample;[1]

(2) the angular dependence of Bragg-scattering,[2] and (3) the wave-

length of maximum reflection.[3] The present paper reports a simple

method for determining the pitch based on transmission measurements.

It can be particularly valuable in the infrared, i.e. a pitch range

of about 0.5 to 5µ , where reflectance measurements are difficult.

A cholesteric liquid crystal characterized by a helix

pitch Z can reflect light of a wavelength $\lambda_r \leq n(\lambda_r)Z$ where n denotes

the refractive index.[3-5] In particular $\lambda_r = n(\lambda_r)Z$ if a parallel

light beam propagating parallel to the helix axis is used for the

measurement. The latter condition is easily fulfilled with a

cholesteric phase displaying the plane texture, where alignment of

the helix axis perpendicular to the supporting surfaces is maintained

throughout the bulk of the sample by wall forces. The reflectivity

arises from the fact that a light beam encounters a change in the

refractive index when passing subsequent cholesteric layers which

are twisted by a certain angle, except when its electric vector rotates

in a sense identical with the screw-sense of the helix. Therefore, a

circularly polarized wave of opposite rotational sense to the helix experiences the strongest reflection. Interference causes the effect to be most pronounced at λ_r = nZ. This allows determination of the pitch from the color of the reflected light. The present paper, however, shows that the change in transmittance near λ_r as a result of reflection can also be used as a simple and reliable probe for obtaining absolute values of Z. This change in transmittance due to the helical structure will be referred to as helical absorption, although it must be understood that this is not a true absorption of energy.

All experiments were done with a 1.75:1.00 mixture of holesteryl chloride and cholesteryl myristate (CM). Previous measurements of the optical rotatory power[6] have shown that its pitch is highly temperature sensitive following the relationship $Z(T) = (4.0 \pm 0.2) \times 10^{-3}/(T-T_{nem})$ (1) for T < 50° with T_{nem} = 40.0°. A 1 mil sample[7] displaying the plane texture was prepared between NaCl windows and inserted into a temperature controlled optical cell. The infrared transmittance was recorded with a Perkin-Elmer 621 IR Spectrophotometer using unpolarized light. It shows a temperature sensitive absorption peak with a half width $\delta\lambda = (0.1 \pm 0.01)\lambda_r$ superimposed on a background absorption arising from vibrational excitation and light scattering.[8] (Figs. 1 and 2). Analyzing 15 absorption curves and calculating Z(T) from the wavelength λ_r of the absorption peaks, using $Z = \lambda_r/n$ and $n(\lambda_r)$ = 1.4, yields pitch values deviating by not more than ±5% from the values derived from measurements of the optical rotatory power (eq. 1). This proves that optical "absorption" of the helical structure is observed. For application

- 2 -

purposes the method is limited to $Z \lesssim 6$ because the IR spectrum is dominated by molecular vibration for $\lambda \gtrsim 8$. Quantitative analysis of the spectra (Fig. 2) shows that a dimensionless "absorption" coefficient α_h per cycle of the helical structure can be defined: $\alpha_h = (3 \pm 1) \times 10^{-2}$. A layer of thickness d containing $N = d/Z$ cycles has the optical density $D = \alpha_h N$.[9]

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7. 1 mil appears to be an optimum layer thickness for a cholesteric structure with $2 < Z < 7\mu$: with $d \geq 2$ mil, the plane texture is no longer perfect, giving rise to a broadening of the absorption peak; with $d \leq 10\mu$ the absorption becomes too weak.

8. The absorption curve of the isotropic melt can be used as a reference line if one corrects for the reduced Rayleigh-scattering.

9. Unpolarized light can be regarded as a superposition of two linear polarized waves of equal intensity both of which can be divided into a right- and left-handed circular component. For light polarized circularily and opposite to the helical sense o has therefore to be multiplied by a factor of 2.

<u>Figure Captions</u>

Figure 1: IR transmittance of CM at various temperatures

(scale expansion x 2).

Figure 2: Helical absorption bands of CM at various temperatures.

The dashed regions correspond to wavelengths where helical

"absorption" is masked by strong vibrational absorption.

The arrows indicate the position of the maxima calculated
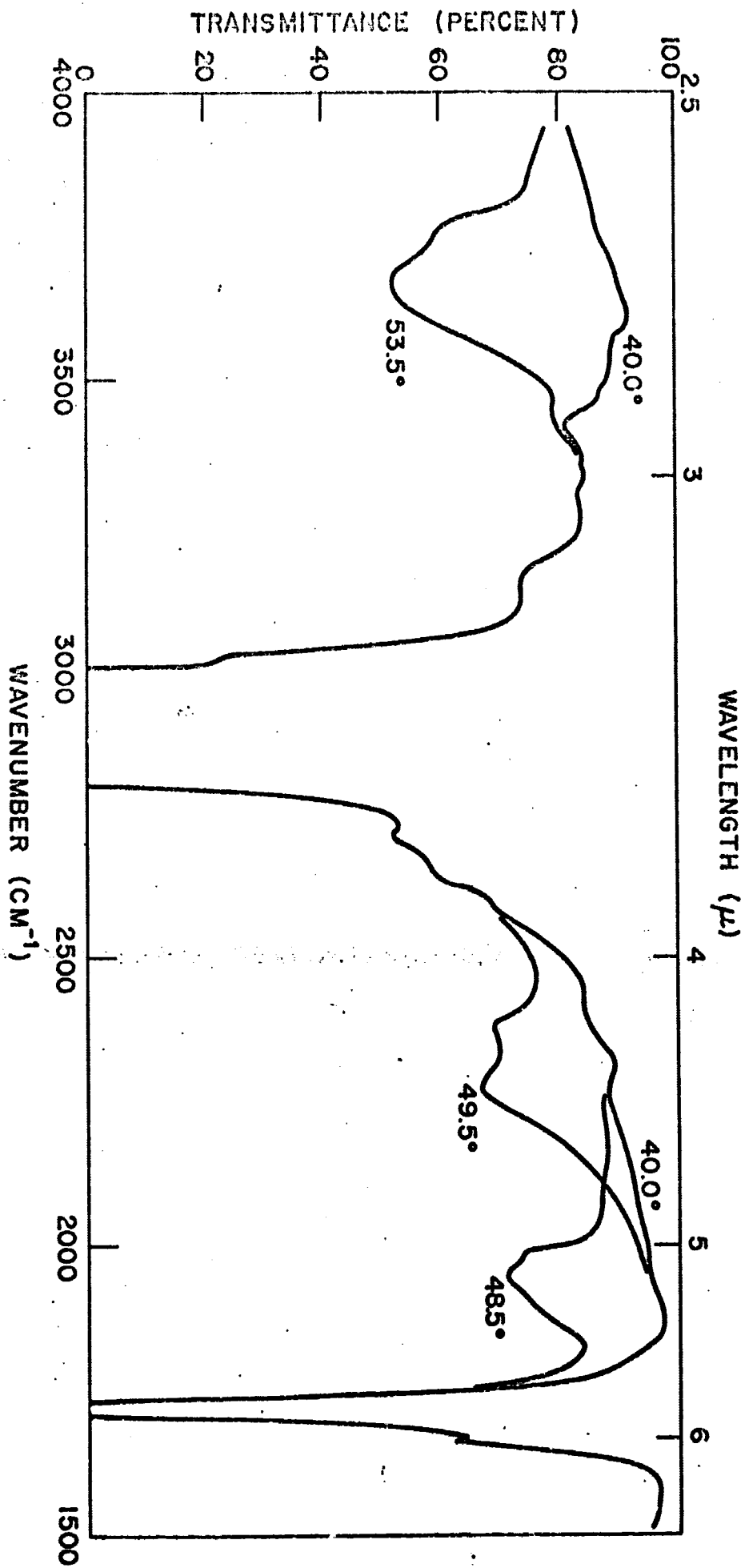
from measurements of the optical rotatory power.
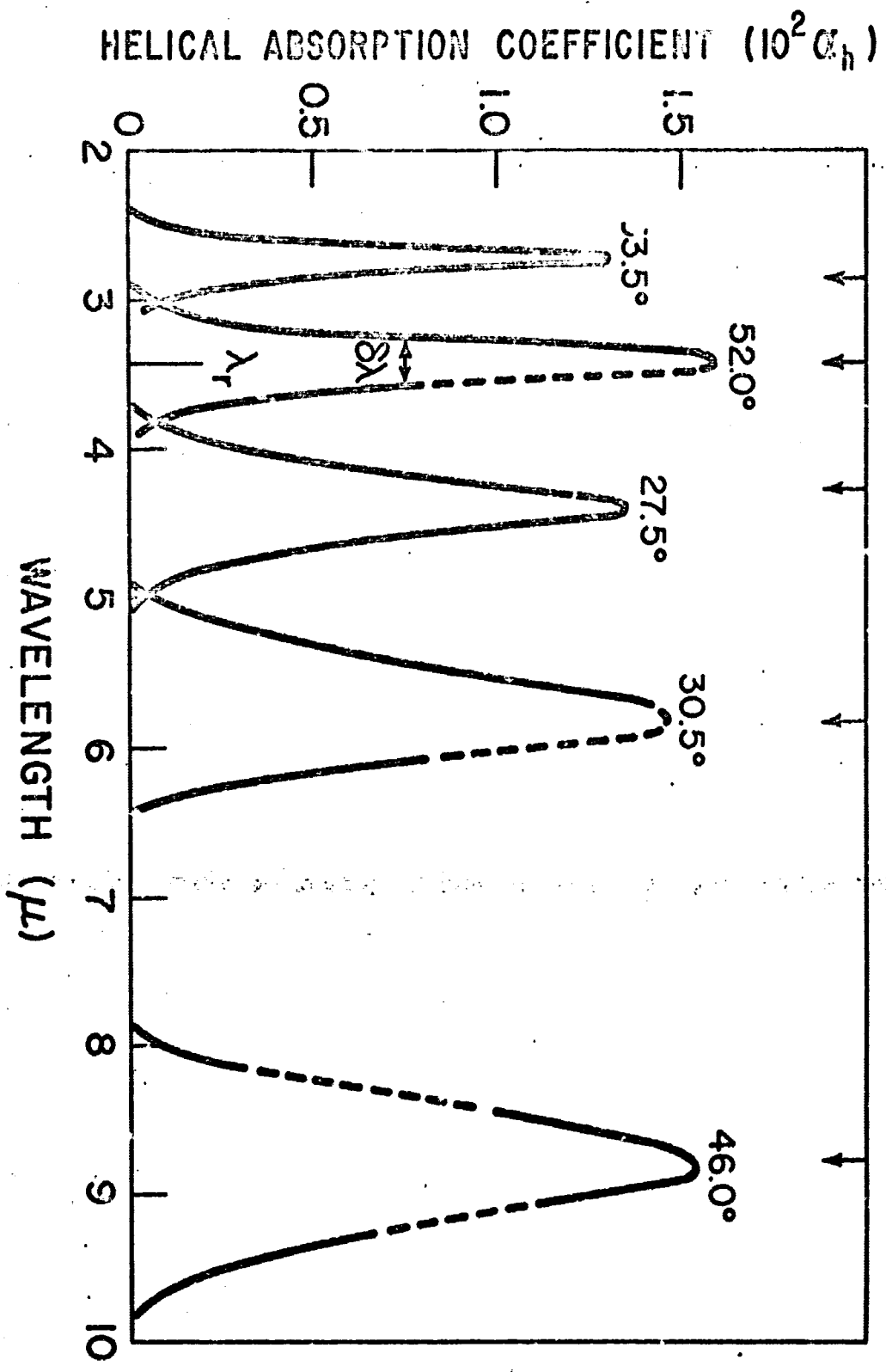
Figure 1

Figure 2