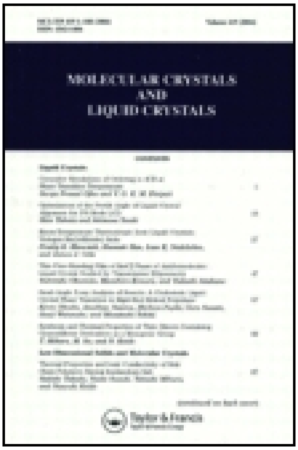

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# Vibrational Spectra of Sterol and Non-sterol Cholesterogens

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Vibrational spectra of sterol cholesterogens, cholesteryl nonanoate (CN), cholesteryl linoleate (CL) and cholesteryl linolenate (CLn) and the non-sterol cholesterogen(+)-2-methyl butyl-(p-(p-methoxy benzylidene) amino) cinnamate (MBMBAC) are discussed. The infrared (IR) spectra of CN, indicates that the intense skeletal in-plane vibrations of (C═C) bond and bending vibrations due to methyl groups in the cholesterol ring system in the smectic A phase are responsible for the formation of spherulites in the solid phase, during cooling. Vibrational spectra of CL and CLn show that an increase in the unsaturation endows greater rigidity to part of the chain. IR spectra of CL confirms the smectic polymorphism exhibited by this compound (above and below 21°C) and also show that both liquid crystalline phases have smectic A like structure. Vibrational spectra of MBMBAC, obtained in different liquid crystalline phases exhibited by the compound are similar. Appearance of the band corresponding to the asymmetric vibrations due to the asymmetric centre in the supercooled smectic B phase of the compound even at a very low temperature, shows that these vibrations are effective in twisting the molecules in each layer, thus forming a twisted smectic B phase at lower temperatures. Greater mobility of the chain and relatively weaker intermolecular interaction within the layer, at higher temperatures give rise to usual smectic B structure. This is in conformity with our observations of density measurements. The intensity of the $CH_3$—O stretching vibrations has been found to be maximum in the smectic A phase of MBMBAC, indicating that the component of the dipole moment acting along the long molecular axis may also be responsible for the smectic-cholesteric transition in this compound.

## I. INTRODUCTION

The study of the vibrational spectra (Infrared and Raman) of liquid crystals is of great interest because they provide information regarding the characteristics of different mesophases and also about the intermolecular interactions in the mesophases.[1-3] The first systematic infrared (IR) spectroscopic study of liquid crystals was done by Maier and Englert.[4,5] They determined the order parameter ($S_2$) of the first seven members of the homologous series, 4,4′-di-alkoxy azoxy benzenes, 2,4-nonadiene, 2,4-decaliene and 2,4-undecaliene acids and also assigned most of the vibrational modes observed in the IR spectra. Bulkin et al.,[6] have studied the IR spectra of p-butyl-n-(p-methoxy benzylidene) aniline (MBBA). Their frequency analyses of the IR spectra were aided by the examination of homeotropically and homogeneously aligned samples of MBBA. Konstantinov et al.,[7] Kelker et al.,[8] and Fernandes and Venugopalan[9] have made measurements of dichroic ratio as a function of temperature. Rajalakshmi et al.,[10] have studied the IR spectra of p-(p-ethoxy phenylazo) phenyl alkanoates, in the solid phase and have made an attempt to correlate the intensities and frequency shifts with crystal structures.

Vibrational spectra of cholesterogens have not been studied as widely as nematogens. It was only in 1975, Fleury and Vergoten[11] presented the spectra of a number of cholesteric compounds in the low frequency region, after L'vova and Sushchinskii[12] reported the spectra of cholesteryl propionate in 1963. Shivaprakash et al.[13] have made IR studies of cholesteryl alkyl carbonates in their solid phase.

Variation of the intensity with temperature, and the frequency shifts in different mesophases of cholesteryl liquid crystalline compounds have not been studied in detail. We present in this paper vibrational spectroscopic studies of different phases of cholesteryl nonanoate (CN), of the smectic phases of cholesteryl linoleate (CL), and of the solid phases of cholesteryl linolenate (CLn). IR studies on the mesophases of a non-sterol cholesterogen, (+)-2-methylbutyl-(p-(p-methoxy benzylidene)amino)cinnamate (MBMBAC), which have been made for the first time are also presented.

## 2. EXPERIMENTAL

The IR spectra were obtained on a Perkin-Elmer 682, Infrared Spectrophotometer equipped with LiF, NaCl and KBr prisms, providing a spectral range of 400–4000 $\mathrm{cm}^{-1}$. The spectra were recorded at different temperatures using Specac 20-100 Temperature Controller and were recorded in the transmission mode on charts of 10 cm width. The charts were self-calibrated for every 10 $\mathrm{cm}^{-1}$ and 20 $\mathrm{cm}^{-1}$. The spectra were obtained with the sample placed between silver chloride (AgCl) plates. Nujol was used as the mulling medium for CN, CLn and MBMBAC, and the spectra of CL were recorded without the mulling medium, as it exhibits smectic phase at 25°C.

The transition temperatures of the samples, under investigation are given below:

CN:

$$\begin{tikzcd}
\text{Solid} \arrow[r, "80^\circ\text{C}"] & \text{Cholesteric} \arrow[r, leftrightarrow, "92.4", "76^\circ\text{C}"'] \arrow[d] & \text{Isotropic} \\
\text{Solid II} \arrow[u] & \text{Smectic A} \arrow[l, "40^\circ\text{C}"'] &
\end{tikzcd}$$

CL:

$$\begin{tikzcd}
 & \text{Solid} \arrow[r, "42^\circ\text{C}"] & \text{Isotropic} \arrow[dr] & & \\
\text{Smectic } A_2 \arrow[ur, "10.5^\circ\text{C}"] & \text{Smectic } A_1 \arrow[l, "21^\circ\text{C}"] & & \text{Cholesteric} \arrow[ll, "30^\circ\text{C}"] & {} \arrow[l, "35^\circ\text{C}"]
\end{tikzcd}$$

CLn:

$$\begin{tikzcd}
\text{Solid I} \arrow[r, "23.1^\circ\text{C}"] & \text{Solid II} \arrow[r, "60^\circ\text{C}"] & \text{Isotropic} \arrow[dl, "48^\circ\text{C}"] \\
\text{Smectic} \arrow[u, "35^\circ\text{C}"] & \text{Cholesteric} \arrow[l, "45^\circ\text{C}"] &
\end{tikzcd}$$

$$\begin{tikzcd}
\text{MBMBAC: Solid} \arrow[r, "53^\circ"] & \text{Smectic B} \arrow[r, leftrightarrow, "58^\circ\text{C}"] & \text{Smectic A} \arrow[dl, leftrightarrow, "78^\circ\text{C}"'] & \\
 & \text{Cholesteric} \arrow[r, leftrightarrow, "98.5^\circ\text{C}"] & \text{Isotropic} &
\end{tikzcd}$$

The IR spectra of CN and MBMBAC were recorded in the solid phase at 16°C and 18°C respectively and in isotropic and other phases during cooling of the samples. The vibrational spectra of CL were recorded at 27.5°C and 18°C, and those of CLn at 18°C and 30°C. Relative intensities and assignment of frequencies are shown in Tables I to IV and the spectra are reproduced in Figures 1 to 7.

## 3. OBSERVATION AND DISCUSSION

### (a) Infrared spectra of cholesteryl nonanoate

The infrared spectrum of CN obtained in the solid phase (Figure 1) is similar to the spectra of cholesteryl laurate[14] except for the shift in the frequencies of some of the bands. For example, the vibrational

TABLE I

Frequencies and assignments for the vibrational spectra of cholesteryl nonanoate

| Band wave number cm$^{-1}$ 1 | Band wave length (μm) 2 | Solid phase at 18°C 3 | Isotropic phase at 95°C 4 | Cholesteric phase at 85°C 5 | Smectic A phase at 65°C 6 | Smectic A phase at 45°C 7 | Assignment 8 |
|---|---|---|---|---|---|---|---|
| 1) 2700–3100 | — | s | s | s | s | s | C—H stretching |
| 2) 1745 | — | v.s<br>(sharp) | v.s | s | s | s | ν(C=O) |
| 3) 1630 | — | — | w | m | s | s | $\beta_{skel}$(C=C) |
| 4) 1595 | — | — | w | m | s | s | |
| 5) 1580 | — | — | w | m | s | s | |
| 6) 1517 | — | — | w | m | s | s | |
| 7) 1470 | — | v.s | v.s | v.s | v.s | v.s | $\partial_{asy}(CH_3)$; $\partial_{asy}(CH_2)$ |
| 8) 1425 | — | — | sh | m | m | m | Chol. $(CH_3)$ |
| 9) 1380 | — | · | v.s | v.s | v.s | v.s | $\partial_{sym}(CH_3)$; Nujol |
| 10) 1312 | — | v.w | — | m | s | s | β(C—H) |
| 11) 1255 | — | m | m | s | v.s | v.s | β(C—H) |
| 12) 1205 | — | — | sh | m | m | m | w$(CH_2)$ |
| 13) 1170 | — | s | s<br>(1165) | s<br>(1165) | s<br>(1165) | s<br>(1160) | β(C—H) |
| 14) 1110 | — | m | m | s | s | s | τ$(CH_2)$ |
| 15) 1030 | — | m | w | m | m | m | γ(C—O) |
| 16) 1012 | — | m | w | w | w | w | β(C—C) |
| 17) 980 | — | v.w | w | m | m | m | |
| 18) 890 | — | v.w | w | m | m | m | r(C—H) |
| 19) 840 | — | v.w | m<br>(835) | s<br>(838) | v.s<br>(835) | v.s<br>(835) | r(C—H) |
| 20) 800 | — | m | — | — | — | — | r(C—H) |
| 21) 767.5 | — | v.w | w | m | m | m | r$(CH_2)$ |
| 22) 722 | — | m | w | w | w | w | r$(CH_2)$ |
| 23) 605 | — | v.w | w | m | m | m | φ(C—C) |
| 24) 545 | — | — | w | m | s | s | (C—C) stretching |

TABLE II

Frequencies and assignments of vibrational spectra of cholesteryl linoleate

| Band wave number $cm^{-1}$ | Intensity | Assignment |
|---|---|---|
| 1. 3470 | broad | (C—O) overtone |
| 2. 2830–3000 | s | (C—H) stretching |
| 3. 1740 | s | $\nu$(C=O) |
| 4. 1680 | w | $\beta_{ske}$ (C=C) |
| 5. 1470 | s | $\partial_{asy}(CH_3)$; $\partial_{asy}(CH_2)$ |
| 6. 1420 | v.w | $\partial_{sym}(CH_2)$ |
| 7. 1380 | m | $\partial_{sym}(CH_3)$ |
| 8. 1250 | w | |
| 9. 1175 | s | β(C—H) |
| 10. 1090 | v.w | |
| 11. 1030 | w | $\nu$(C—O) |
| 12. 1015 | m | $\nu(CH_3)$, β(C—H) |
| 13. 725 | m | $r(CH_2)$ |

frequency of the carbonyl (C=O) group in cholesteryl laurate (1680 $cm^{-1}$) has shifted to 1745 $cm^{-1}$ in CN. This may be due to the fact that carbonyl group in cholesteryl laurate is attached to a longer chain, compared to that in CN, which affects the coplanarity with the benzene ring.

Another important observation in the solid phase spectra of CN is the absence of vibrations in the range 1500–1640 $cm^{-1}$ and at 1425 $cm^{-1}$. The former are due to the skeletal in-plane deformation of C=C in the steroid ring system and the latter due to bending vibrations of the methylene group in the steroid ring system. It is known

TABLE III

Frequencies and assignments for the vibrational spectra of Cholesteryl linolenate

| Band wave number $cm^{-1}$ | Intensity | Assignment |
|---|---|---|
| 1. 2800–3000 | broad | (C—H) stretching |
| 2. 1600–1800 | broad | $\nu$(C=C) and $\nu$(C=O) |
| 3. 1440–1470 | s | $\partial_{asym}(CH_3)$; $\partial_{asym}(CH_2)$ |
| 4. 1380 | s | $\partial_{sym}(CH_3)$; Nujol |
| 5. 1310 | v.w | β(C—H) |
| 6. 1170 | v.w | |
| 7. 975 | v.w | ∂(C—H) |
| 8. 720 | s | $r(CH_2)$ |

TABLE IV

Frequencies and assignments of the vibrational spectra of (+)-2-methyl butyl-(p-(p-methoxy benzylidene) amino) cinnamate [MBMBAC]

| Band wave number $cm^{-1}$ 1 | Solid phase at 18°C 2 | Isotropic phase 100°C 3 | Cholesteric phase 87.5°C 4 | Smectic A phase 65°C 5 | Smectic B phase 45°C 6 | Smectic B phase 18°C 7 | Assignment 8 |
|---|---|---|---|---|---|---|---|
| 1) 2800–3100 | s | s | s | s | s | s | (C—H) stretching |
| 2) 1720 | s | s | s<br>(broad) | v.s | v.s | v.s | $\nu$(C=O) |
| 3) 1640 | s | s | s | s | s<br>(1630) | s<br>(1630) | $\nu$(C=N) |
| 4) 1595 | s | v.s | v.s. | v.s. | s | m | $\nu(C=C)_{arom}$ |
| 5) 1580 | m | v.s | v.s | m | m | w | $\nu(C=C)_{arom}$ |
| 6) 1520 | m | v.s | v.s | v.s | v.s | v.s | β(C=C) |
| 7) 1460 | v.s | v.s | v.s | v.s | v.s | v.s | $\partial_{asy}(CH_3)$; $\partial_{asy}(CH_2)$ |
| 8) 1420 | w | s | v.s | s | m | m | C—$CH_3$ asym.deform |
| 9) 1380 | v.s | v.s | v.s | v.s | v.s | v.s | $\partial_{sym}(CH_3)$; Nujol |
| 10) 1305–1340 | s | v.s<br>(1310) | v.s<br>(1310) | v.s | v.s | v.s | β(C—H) |
| 11) 1255 | s | v.s | v.s<br>(1250–1265) | v.s<br>(1250–1262) | v.s | s | $\nu$(C—O) |
| 12) 1205 | s | v.s | v.s | v.s | s | s | β(C—H) |
| 13) 1165 | s | v.s | v.s | v.s | v.s<br>(1160) | v.s<br>(1160) | $\nu(CH_3—O)$ |
| 14) 1105 | v.w | s | v.s | m | m<br>(1110) | m<br>(1110) | $\tau(CH_2)$ |
| 15) 1035 | m | s | s | s | m | m | $\nu$(C—C) |
| 16) 985 | m | s | s | s | s | s | R |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 17) | 890 | m | s | s | s | m<br>(885) | m | $\gamma$(C—H) |
| 18) | 835 | s | v.s | v.s | v.s | v.s | v.s | Out of plane deformation of the phenyl ring |
| 19) | 765 | m | — | — | vvw | m | m | $\gamma$(C—C); $\gamma(CH_3)$; $\gamma(CH_3)$ |
| 20) | 722 | m | — | — | — | v.w | m | $\gamma$(C—H); $\gamma(CH_3)$ |
| 21) | 630 | m | — | — | — | — | w | Chain |
| 22) | 605 | s | w | w | m | s | s | $\phi$(C—C) |
| 23) | 550 | v.s | m | m | s | v.s | v.s | (C—C) stretching |
| 24) | 485 | m | — | — | — | w | w | $\partial$(C—C) |

$\nu$(C=O) : C=O stretching
$\beta_{sks}$(C=C) : C=C skeletal in-plane deformation in benzene
$\nu$(C—C) : C—C skeletal stretch
$\partial_{sym}(CH_2)$ : $CH_2$ symmetric deformation vibration
$\partial_{sym}(CH_3)$ : $CH_3$ symmetric deformation vibration
$\beta$(C—H) : C—H in-plane deformation
$\partial$(C—H) : C—H deformation vibration
$\partial_{asy}(CH_3)$ : $CH_3$ asymmetric deformation vibration
$\partial_{asy}(CH_2)$ : $CH_2$ asymmetric deformation vibration
$\beta$(C—C) : C—C in-plane deformation
$r(CH_2)$ : $CH_2$ rocking deformation
$r_p(CH_3)$ : $CH_3$ out of plane rocking
$\gamma$(C—H) : C—H out of plane deformation
$r(CH_3)$ : $CH_3$ rocking
$\nu$(C—O) : C—O stretching
$\omega(CH_2)$ : $CH_2$ wagging
$\phi$(C—C) : out of plane ring deformation
R : Coupled skeletal and $CH_3$ in-plane rocking
$\tau(CH_2)$ : Twisting modes of methyl groups of the chain.

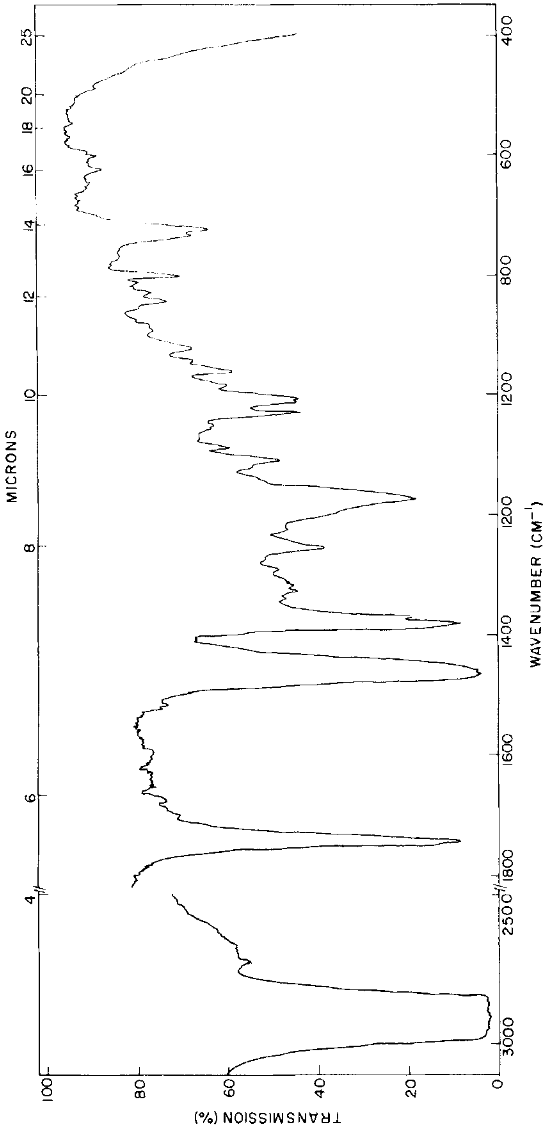

FIGURE 1 Percentage transmission versus wavelength in the solid phase (at 18°C) of cholesteryl nonanoate.

from the crystal structure analysis that CN and its related structures[15–17] show close packing of tetracyclic systems for antiparallel arrangement of molecules, and the projecting methyl groups of the steroid ring system have an interlocking effect. This can explain the absence of vibrations corresponding to 1425 $cm^{-1}$. As the steroid ring systems are tightly bound to one another, the vibrations corresponding to skeletal in-plane deformation of C═C are absent. The rocking vibrations due to nonanoate chain splits into two components (722 $cm^{-1}$ and 732 $cm^{-1}$) in the solid phase, as in the case of n-paraffins, fatty acids and other long chain polymethylene compounds.[18–20] Due to the high mobility of the nonanoate chains (in the solid phase), small wagging and twisting motions associated with trans arrangement of methylene groups may be present. These may be assigned to the band at 1110 $cm^{-1}$.[21]

The band corresponding to the carbonyl group (C═O), which is sharp in the solid phase, broadens in the cholesteric and smectic phases. This broadening is due to the coupling of vibrational modes.[22]

The four bands at 1517 $cm^{-1}$, 1580 $cm^{-1}$, 1595 $cm^{-1}$ and 1630 $cm^{-1}$, are assigned to the C═C skeletal in-plane vibrations. These bands are shown separately in Figure 2 to compare their intensities in different phases. Similarly, the band at 1425 $cm^{-1}$ which is assigned to the bending vibrations of methyl groups in the steroid ring system, is also shown in Figure 2. The band at 1110 $cm^{-1}$, assigned to twisting mode of methyl groups of nonanoate chain, increases in intensity as temperature decreases. Only one component of the rocking vibration (at 722 $cm^{-1}$) is observed in isotropic and liquid crystalline phases.

### (b) Formation of spherulites in the solid phase of cholesteryl nonanoate

Figure 2 shows that the intensities of C═C skeletal in-plane vibrations and of bending vibrations of the methyl groups in the steroid ring system, increase as the temperature decreases. They are more intense near the smectic A-solid transition temperature (45°C), and are absent in the solid phase. These indicate the advent of a new type of solid phase. The methyl groups of the steroid ring system have been found to be responsible for the rotation in the cholesterol derivatives.[23] The intense (C═C) skeletal in-plane vibrations show that the bonding between the molecules is relatively weak. Hence, the solid formed does not possess the regular structure of solid phase in which these vibrations were absent. We refer to this phase formed on cooling, as solid II. The optical observations confirm that CN nucleates in the

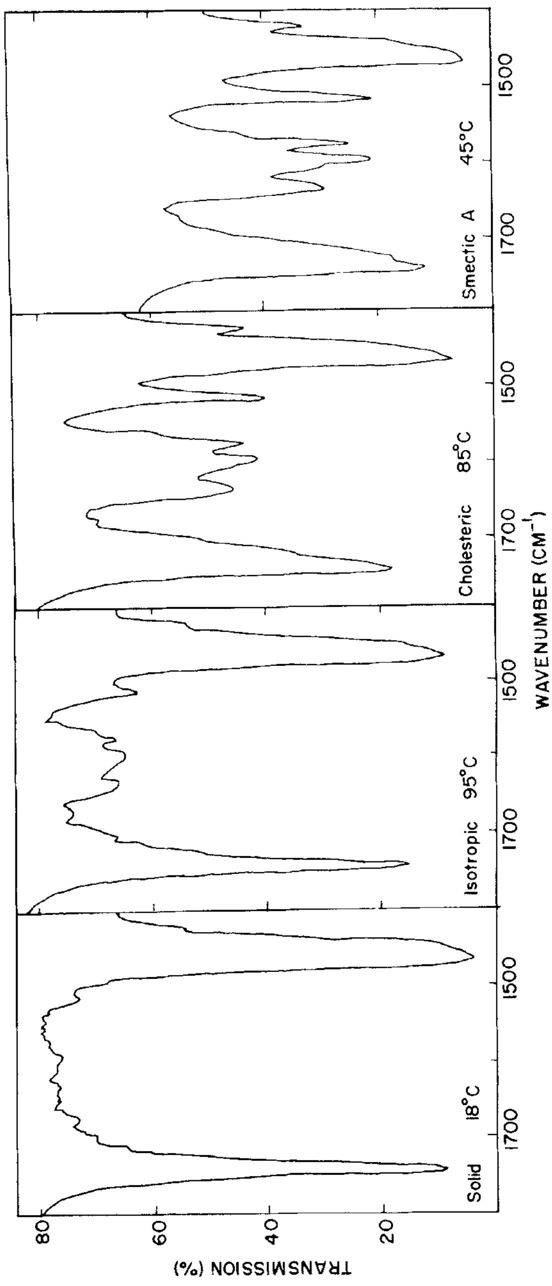

FIGURE 2 Percentage transmission versus wavelength of skeletal in-plane vibrations of (C=C) and bending vibrations of the methylene group in the steroid ring system in solid, isotropic, cholesteric and smectic A phases of cholesteryl nonanoate.

form of spherulites during cooling. Therefore the formation of spherulites in the solid phase is responsible for the intense (C=C) skeletal in-plane vibrations and bending vibrations of methyl groups in the steroid ring system, near the smectic A-solid transition.

### (c) Infrared spectra of cholesteryl linoleate

Number of vibrational bands appearing in the smectic phase of CL (Figure 3) is less than the number appearing in CN indicating that many of the vibrations are restricted due to the presence of two cis double bands in the linoleate chain. The stretching vibration due to the carbonyl (C=O) group differs only by 5 $cm^{-1}$ from that of CN. But β(C=C) and $\partial(CH_3)$ due to methyl groups in the steroid ring system are very weak compared to those in the smectic A phase of CN. This indicates that the twisting power of the cholesterol ring system is lower than that of CN as the long linoleate chain restricts such vibrations. The band corresponding to the wave number 725 $cm^{-1}$ is assigned to the rocking vibrations of $CH_2$ group. Shivaprakash et al.,[13] have observed two frequencies at 729 $cm^{-1}$ and at 716 $cm^{-1}$ corresponding to $r(CH_2)$ in cholesteryl oleyl carbonate. They have attributed this splitting of rocking vibrations of $CH_2$ groups to the interaction between the two vibrating units of $(CH_2)_7$ at equal distances from CH=CH bond, in the side chain of cholesteryl oleyl carbonate. The presence of two cis double bonds in the lineoleate chain makes the vibrating units unequal, and the vibrations of the longer unit (part of the chain between the double bonds and the cholesteryl ring system) predominate.

### (d) Infrared spectra of cholesteryl linoleate at 18°C

Infrared spectra of CL, obtained at 18°C, show no change (Figure 3) except for the variation in the intensity of bands. This confirms our earlier result[24] that the additional smectic phase formed below 21°C is also of smectic A type, but with a closer packing of molecules.

### (e) Infrared spectra of cholesteryl linolenate in the solid phase

Absence of band corresponding to the carbonyl (C=O) group is conspicuous in the vibrational spectra of CLn (Figure 4). Instead, a broad weak band appears in the region 1600–1800 $cm^{-1}$. The stretching vibrations due to the carbonyl group are very weak because of the presence of three cis double bonds in the linolenate chain. These three unsaturated bonds make the linolenate chain to get rigidly

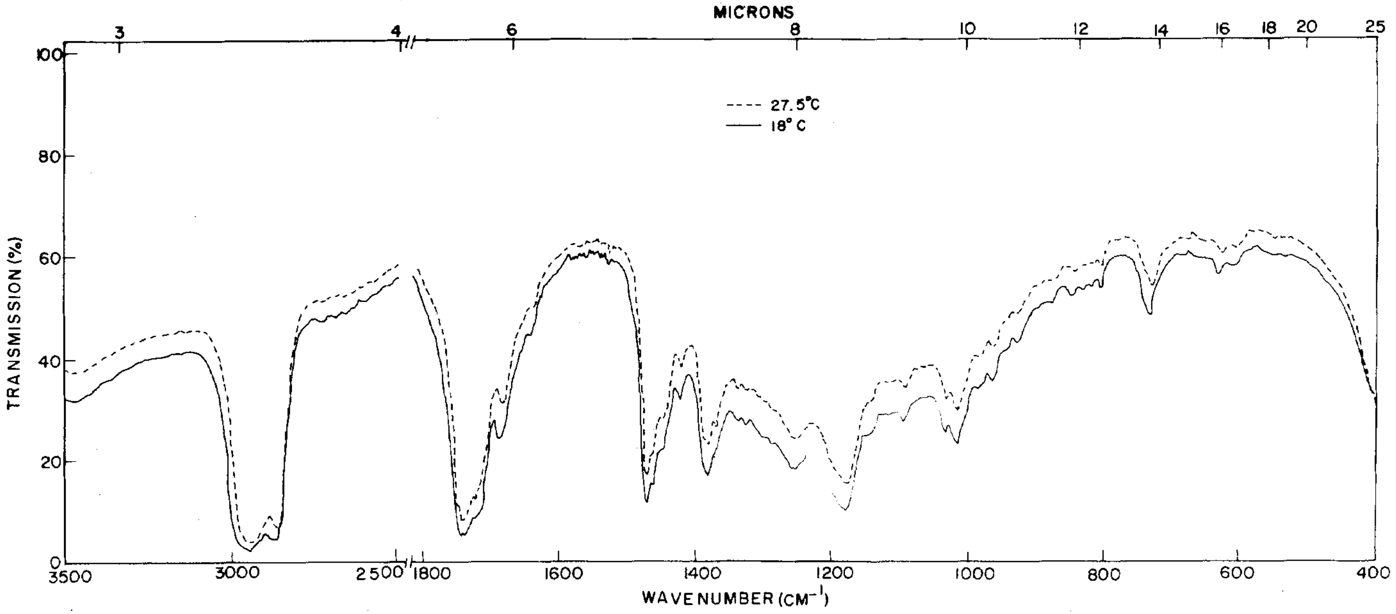

FIGURE 3 Percentage transmission versus wavelength in the smectic $A_1$ (at 27.5°C, and in the smectic $A_2$ (at 18°C) phases of cholesteryl linoleate.

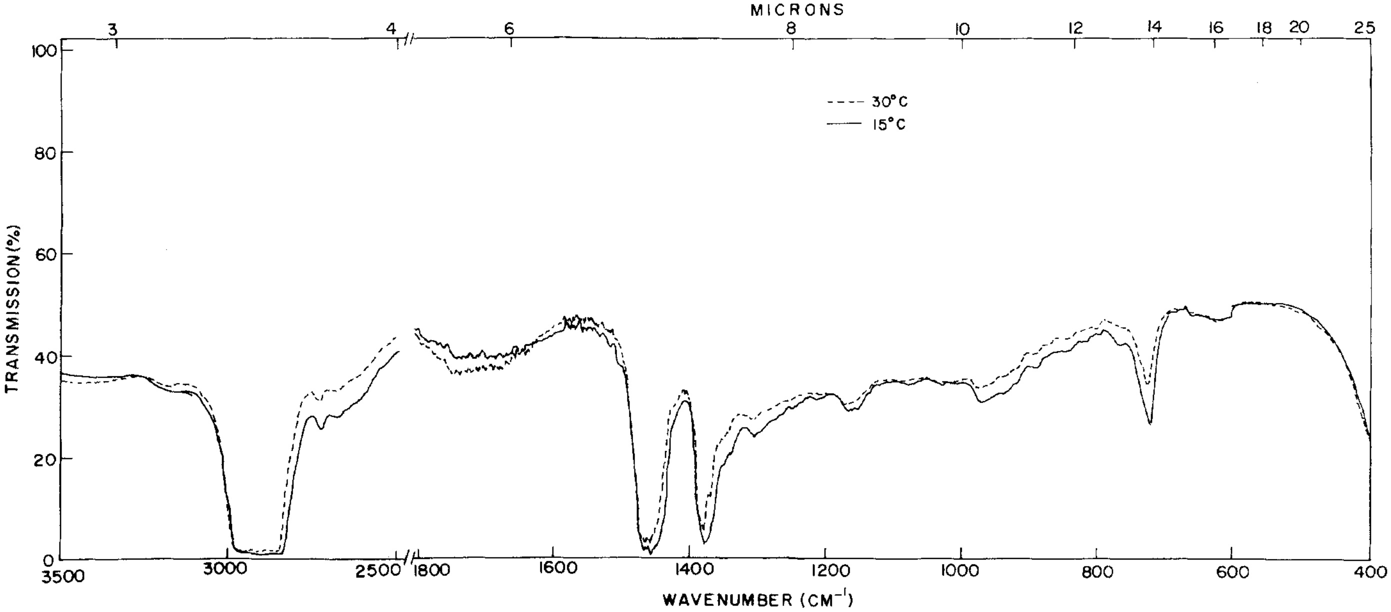

FIGURE 4 Percentage transmission versus wavelength in the solid I (at 18°C) and solid II (at 30°C) phases of cholesteryl linolenate.

attached to the cholesteryl ring system, weakening the C═O stretching frequency. The in-plane vibrations of (C—H) groups and the (C═C) skeletal in-plane vibrations are very weak compared to those observed in the CL molecule. Jackson et al.[25] have reported a weak band with a maximum at 910 $cm^{-1}$ (10.95 microns) in the spectra of non-conjugated cis-cis-linoleate (in the isomers of methyl linoleate). They have assigned this band to the olefinic (C—H) bending deformation. Similarly, a weak band appearing at 975 $cm^{-1}$ in the spectra of CLn may be assigned to the (C—H) bending deformation of the cis-cis-cis-linolenate chain. The band at 720 $cm^{-1}$ is assigned to the rocking vibrations of $CH_2$ groups. The intensities of these bands are stronger as compared with those of linoleate chain. The rocking vibrations in CLn are entirely due to the part of the linolenate chain between the three cis double bonds and the cholesteryl ring system.

It is found from the thermal studies on CLn that there is a weak exothermic solid-solid transition at 23.1°C while heating the sample. The two spectra obtained at 18°C and 30°C (Figure 4) do not show perceptible structural difference between the two types of solids, except for the change in the intensity of the bands. The broad peak in the region 1600–1800 $cm^{-1}$ is more pronounced at 30°C. This is obviously due to the greater freedom attained by the molecules at higher temperatures.

### (f) Infrared spectra of MBMBAC

The sharp band at 1720 $cm^{-1}$ is assigned to the stretching vibrations of the carbonyl (C═O) group (Figure 5). There are four bands at 1640 $cm^{-1}$, 1595 $cm^{-1}$, 1580 $cm^{-1}$ and 1520 $cm^{-1}$. One of these, corresponding to 1640 $cm^{-1}$ is assigned to the C═N stretching vibration. This may be compared with the C═N stretching frequency (1620 $cm^{-1}$) obtained for MBBA by Bulkin et al.[6] The increase in the stretching frequency of C═N in MBMBAC is due to the presence of different end chain groups. Bands corresponding to 1595 $cm^{-1}$ and 1580 $cm^{-1}$ are assigned to (C═C) aromatic stretching vibrations. There is an additional band at 1520 $cm^{-1}$ in the spectra of MBMBAC, which is assigned to the C═C in-plane deformation present in the cinnamate group.

The spectra of solid, isotropic and liquid crystalline phases of MBMBAC, are very similar except for the variation in the intensity of bands. The band due to the carbonyl group (C═O) broadens in the liquid crystalline phases. This is due to the coupling of vibrations at higher temperatures. Aromatic stretching vibrations also decrease with the decrease of temperature. The band appearing at 1420 $cm^{-1}$

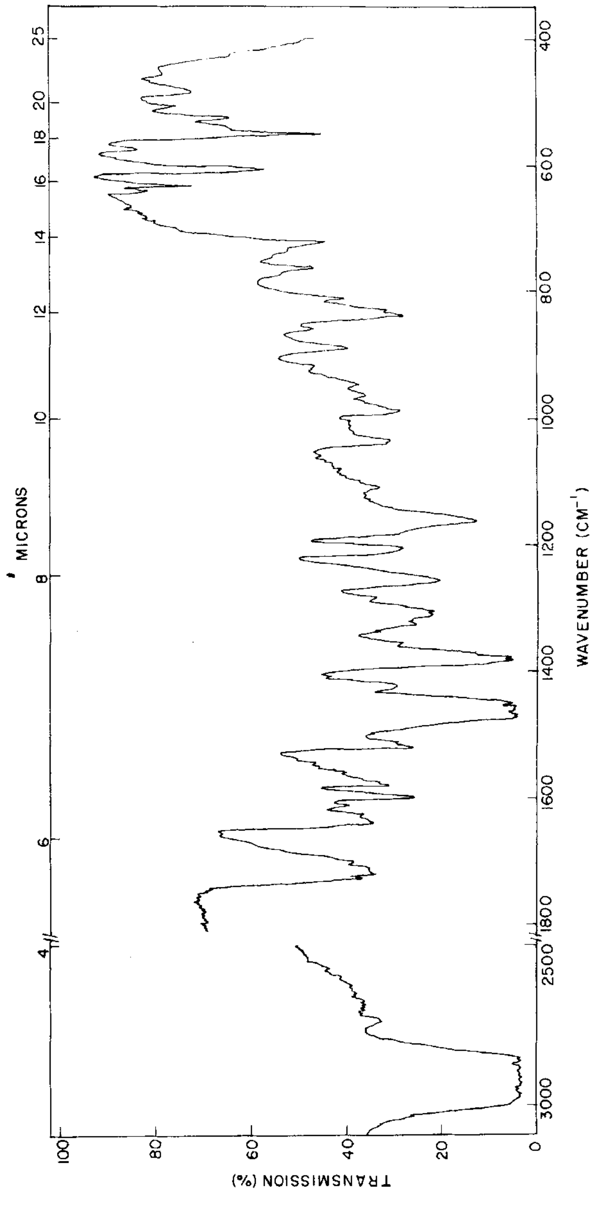

FIGURE 5 Percentage transmission versus wavelength in the solid phase (at 16°C) of MBMBAC.

is assigned to C—$CH_3$ asymmetric deformation due to the asymmetric centre present in the chain of the molecule. The asymmetric deformation due to the asymmetric centre is weak in the solid phase and becomes strong in the isotropic phase. As the temperature is lowered from the isotropic phase, the intensity of these vibrations increase further in the cholesteric phase and gradually decrease in the smectic A and smectic B phases. This shows that the asymmetric centre is responsible for the formation of cholesteric phase in this compound and the twisting effect gradually decreases as the temperature is lowered. The band at 1105 $cm^{-1}$ which is assigned to the twisting of methyl groups in the chain, also shows a similar trend.

### (g) Structure of smectic B phase at higher and lower temperatures

Asymmetric vibrations due to C—$CH_3$ groups and twist deformations due to methyl groups in the chain are more intense in the smectic B phase at higher temperature (45°C) (Figure 6). This shows that these vibrating groups are more free and chains are liquid-like at higher temperatures. Greater intensity of the C=C aromatic stretching vibrations at higher temperatures, also indicates that the intermolecular interactions are relatively weak at higher temperatures. Hence it may be inferred that the smectic B phase formed at higher temperature has the usual structure as described by de Gennes.[26,27]

The intensity of these vibrations in the smectic B phase decrease as the temperature decreases; so also the intensity of the C=C stretching vibrations (Figure 6). These indicate that the coupling between the layers,[28] and the intermolecular interactions within the layer, increase with decrease of temperature. However, the effect of the asymmetric vibrations due to C—$CH_3$ groups cannot be ruled out even at a very low temperature (18°C). The effect of these vibrations at lower temperatures would be to twist the molecules in each layer with respect to the consecutive layers, giving rise to chiral-smectic B phase. This is also in conformity with the fact that the twisted phases are more stable at lower temperatures.[29] Mitra et al.,[30] have observed a gradual change in the structure of smectic B phase of MBMBAC below 58°C in their X-ray studies. Variation of density also indicates that there is a second order-type transition at 40°C. The change from usual type of smectic B to a twisted structure can be of second order-type. Hence such a change is in conformity with the observed facts.

### (h) Effect of dipole moment on the smectic A- cholesteric transition

The band corresponding to $CH_3$—O stretching vibrations in different phases is shown in Figure 7. The band is sharp in the solid and in

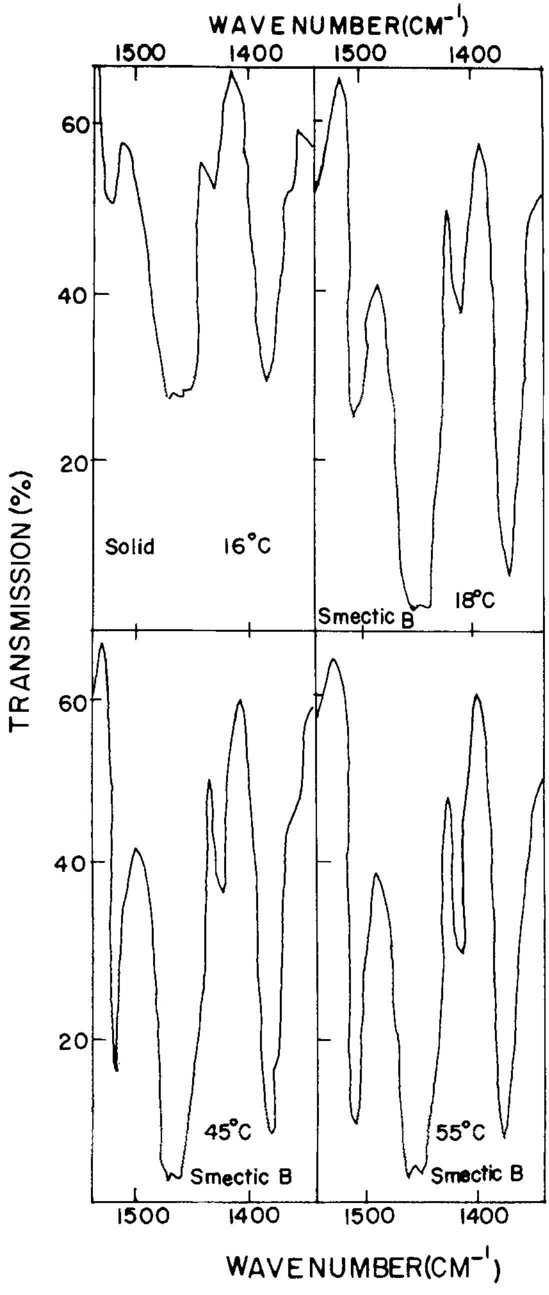

FIGURE 6 Percentage transmission versus wavelength of the C—$CH_3$ asymmetric deformation vibration in solid phase (at 16°C) and at different temperatures in the smectic B phase of MBMBAC.

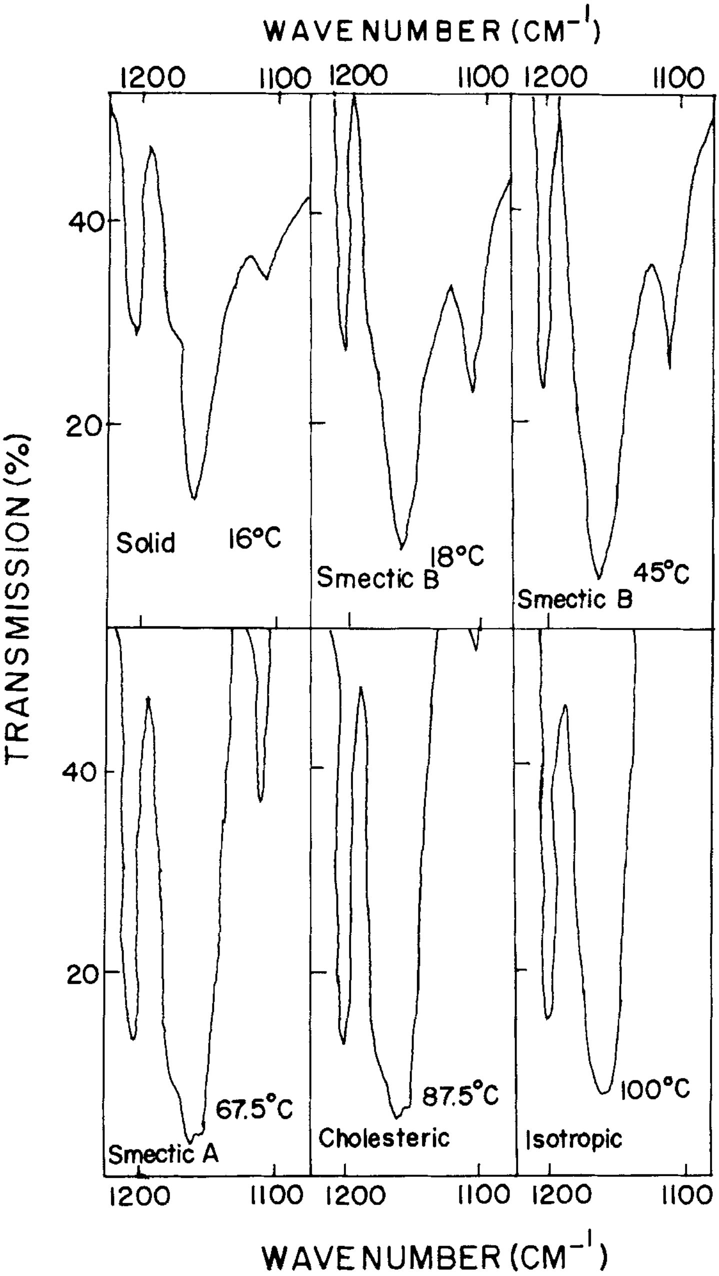

FIGURE 7 Percentage transmission versus wavelength of the $CH_3$—O stretching vibrations in the solid, smectic B (at 18°C and at 45°C), smectic A, cholesteric and isotropic phases of MBMBAC.

smectic B phases, but is broadened in smectic A and in cholesteric phases. It is also observed that its intensity is maximum in the smectic A phase. This can be explained in the following way: MBMBAC is the only member of the 2-methyl butyl-(p-(p-alkoxy benzylidene)amino) cinnamate series, exhibiting cholesteric phase.[31] All other members with ethyloxy($C_2H_5O$), propyloxy ($C_3H_4O$), butyloxy ($C_4H_9O$) etc., are pure smectogens. It has also been shown by Gray[31] that when the terminal substituents are C—N and $NMe_2$ (where Me is the methyl group) instead of alkoxy in the above compound, it is a cholesterogen and smectogen respectively. These facts show that the dipole moment (for example $CH_3$—O in MBMBAC) component acting along the long molecular axis is responsible for the formation of cholesteric phase in these compounds.

The dipole moment in the case of C≡N acts along the long molecular axis. In $CH_3$—O the dipole moment acts at an angle of 57° to the long molecular axis and lies in the plane of the benzene ring. When the terminal substituent is $NMe_2$, the dipole moment acts at an angle of nearly 58° and lies perpendicular to the plane of the benzene ring. In the latter two cases therefore, only a fraction of the dipole moment acts along the long molecular axis. This component appears to influence the movement of molecules in a direction perpendicular to the layers (density wave).[32] The component acting along the long molecular axis in the case of $CH_3$—O is just enough to bring about smectic A-cholesteric transition. When the terminal substituents are $C_2H_5O$, $C_3H_7O$ etc., the additional methyl groups 'insulate' the component acting along the long molecular axis and therefore they are pure smectogens. When the terminal substituent is $NMe_2$, the component acting along the molecular axis may not be enough to bring about smectic-cholesteric transition. Hence it is also a smectogen.

The perpendicular component will also be effective for the two dimensional order in the smectic B phase, whereas in the smectic A phase, the molecules attain greater rotational freedom and the perpendicular component will be less effective because of the liquid-like structure of each layer. Hence, the maximum intensity observed in the vibrational band of $CH_3$—O in MBMBAC is due to the component acting along the long molecular axis.

## 4. CONCLUSION

(i) In the cholesteric phase the skeletal C═C in-plane vibrations and deformational vibrations of methyl groups of the cholesterol skeleton are more intense.

In the smectic A phase of CN the intensity of these vibrations increases as the temperature is decreased, indicating the formation of spherulites in the solid phase.

(ii) Infrared spectra of cholesteryl linoleate at 18°C and at 27.5°C are similar, confirming our earlier result[24] that the additional smectic phase formed below 21°C is of smectic A-type.

(iii) The two solid phases formed by cholesteryl linolenate during heating do not have much difference in their structure.

(iv) Increase in the chain unsaturation increases the rigidity of the part of the chain, between the cis double bonds and the cholesteryl ring system. However, the kink formed due to the double bonds in the chain increases and is mainly responsible for the decrease in the anisotropy with increase in the chain unsaturation. This in turn influences the mesomorphic behaviour of the unsaturated C—18 compounds.

(v) The higher intensity of asymmetric vibrations of $C—CH_3$ group in the cholesteric phase of non-sterol cholesterogen indicates that the asymmetric centre is responsible for the formation of cholesteric phase. As temperature decreases, the intensity of these asymmetric vibrations also decreases. Presence of $C—CH_3$ asymmetric vibrations and the twist deformations of the methyl groups in the chain, in the smectic B phase at 18°C indicate that the phase formed at lower temperatures is chiral-smectic B.

(vi) Component of the dipole moment due to $—CH_3O$ acting along the molecular axis contributes to the formation of cholesteric phase in MBMBAC.

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