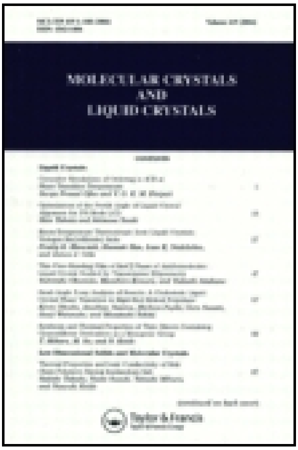

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Vibrational Spectra of Cholesteric Liquid Crystals

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Vibrational Spectra of Cholesteric Liquid Crystals

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Infrared (4000–625 cm^{-1}) and far infrared (20–650 cm^{-1}) spectra of cholesterogenic materials—cholesteryl methyl and ethyl carbonates, benzoate and laurate have been examined in the solid state. Correlation of the variation in the intensities and frequency shifts with the molecular structures shows that the long side chain plays an important role in the stabilization of the cholesteric phase. The shift in the carbonyl frequency in the case of cholesteryl laurate may be correlated with the effect on the coplanarity with benzene due to the extended end chain. This is further confirmed by the effect on the librational mode in far infrared region.

INTRODUCTION

The study of the vibrational spectra of liquid crystals has been of considerable interest in recent years.[1] Infrared absorption and Raman spectra of several liquid crystals have been investigated and have provided useful information regarding the characteristics of the different mesophases. The low modes in these spectra are of particular interest as these are related to the intermolecular forces in liquid crystals. So far, few studies have been reported on the far-infrared spectra of liquid crystals.[2–16]

Cholesteric phases have not been actively investigated from the viewpoint of mesophase structure elucidation via vibrational spectrum unlike other liquid crystalline phases. L'Vova and Sushchinskii[17] had in the early 1960's reported the infrared spectra of cholesteryl propionate. Bulkin and Krishnan[18] have discussed the Raman spectra of a number of cholesteric esters in crystal, cholesteric and isotropic phases, as well as the spectra of mixture of cholesterics. Recently, Fleury and Vergoten[19] have presented the spectra of a number of cholesteric compounds in the low frequency region. Their results in the crystalline phase indicate the presence of a number of low frequency lattice vibrations. In this paper, we present some preliminary results of our study of the absorption of cholesteric liquid crystalline materials in the infrared and far-infrared region.

EXPERIMENTAL

All chemicals were purchased from Eastman Organic Chemicals Division. The samples were recrystallized before use. The infrared spectra were obtained on a Perkin-Elmer 257 infrared spectrophotometer equipped with LiF, NaCl and KBr prisms and providing a recording spectral range of 625–4000 cm^{-1}. The spectra were recorded at room temperature (percentage transmittance versus wave number) on charts of 10 cm width. The spectra were registered with Nujol as mulling medium between KBr plates.

The far-infrared spectra were recorded on Polytec Fourier far-infrared spectrophotometer providing a recording spectral range of 20–650 cm^{-1}. The spectral range of 20–650 cm^{-1} was covered using two different beam splitters.

TABLE I

Cholesteryl benzoate

Band wavelength μm	Band wave number cm^{-1}	Intensity[a]	Assignment[b]
3.39 3.53	2950 2830	vs, Broad	$\nu_{asy}(CH_3)$; $\nu_{asy}(CH_2)$
5.99	1670	s	$\nu(C{=}O)$
6.23	1590	m	$\beta_{ske}(C{=}C)$
6.88	1454	vs	$\delta_{asy}(CH_3)$; $\delta_{asy}(CH_2)$
7.38	1355	s	$\delta_{sy}(CH_3)$
7.46	1340	sh	$\delta(C{-}H)$
7.90	1265	vs	$\beta(C{-}H)$
8.04	1243	sh	$\omega(CH_2)$
8.40	1190	w	$\beta(C{-}H)$
8.58	1165	m	$\beta(C{-}H)$
9.26	1080	sh	$\beta(C{-}H)$
9.76	1025	s	$\nu(C{-}O)$
10.00	1000	m	$\beta(C{-}C)$
10.10	990	m	R
11.24	890	m	$\gamma(C{-}H)$
11.56	865	m	$\gamma(C{-}H)$
11.90	840	m	$\gamma(C{-}H)$
12.58	795	m	$\gamma(C{-}H)$
13.93	718	vs	$r(CH_2)$
14.59	685	w	$\gamma(C{-}H)$
14.71	680	w	$\gamma(C{-}H)$

[a] See footnote in Table VI.
[b] See footnote in Table VI.

One had a usable transmission range of 20–180 cm^{-1} and the other had a range of 100–650 cm^{-1}. The spectra in the two ranges were obtained with resolutions of 5 cm^{-1}. Tables I and II give the corrected band positions, relative intensities and assignments of the frequencies observed in the solid state for cholesteric benzoate and cholesteryl laurate (infrared spectra) and the spectra are reproduced in Figures 1 and 2. Tables III to VI give the assignments of frequency bands in the solid state for cholesteryl benzoate cholesteryl methyl carbonate, cholesteryl ethyl carbonate, and cholesteryl laurate in the far-infrared region and the spectra are reproduced in Figures 3 and 4.

RESULTS AND DISCUSSION

An analysis of the assignment of the spectra reveals that there are no gross changes in either the relative intensities or in the frequencies. Also we do not observe much difference in the frequency assignment for cholesteryl oleyl carbonate[20] as compared with cholesteryl benzoate and cholesteryl laurate even though it is in the liquid crystalline state as observed by Vergoten *et al.*[12] for nematic liquid crystals. This suggests strong dependence of the arrangement of molecules in liquid crystalline state on the previous history of molecular

TABLE II

Cholesteryl laurate

Band wavelength μm	Band wave number cm^{-1}	Intensity[a]	Assignment[b]
3.39 3.53	2950 2830	vs, Broad	$\nu_{asy}(CH_3)$; $\nu_{asy}(CH_2)$
5.95	1680	vs	$\nu(C{=}O)$
6.90	1450	vs	$\delta_{asy}(CH_3)$; $\delta_{asy}(CH_2)$
7.30	1370	s	$\delta_{sy}(CH_3)$
7.90	1265	vw	$\beta(C{-}H)$
8.00	1250	vw	$\beta(C{-}H)$
8.04	1243	w	$\omega(CH_2)$
8.56	1168	s	$\beta(C{-}H)$
9.20	1080	w	$\beta(C{-}H)$
9.80	1020	w	$r(CH_3)$; $\beta(C{-}H)$
9.90	1010	vw	$\beta(C{-}C)$
11.36	880	w	$\gamma(C{-}H)$
11.90	840	w	$\gamma(C{-}H)$
12.58	795	m	$\gamma(C{-}H)$
13.89	720	s	$r(CH_2)$

[a] See footnote in Table VI.
[b] See footnote in Table VI.

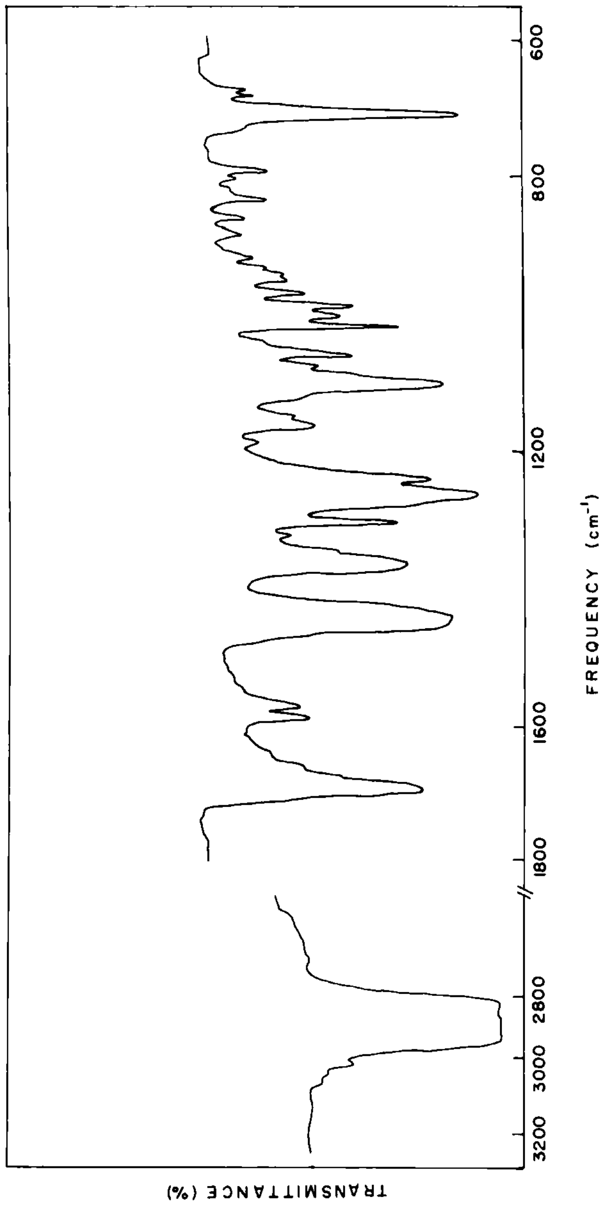

FIGURE 1 Percentage transmittance versus frequency for cholesteryl benzoate.

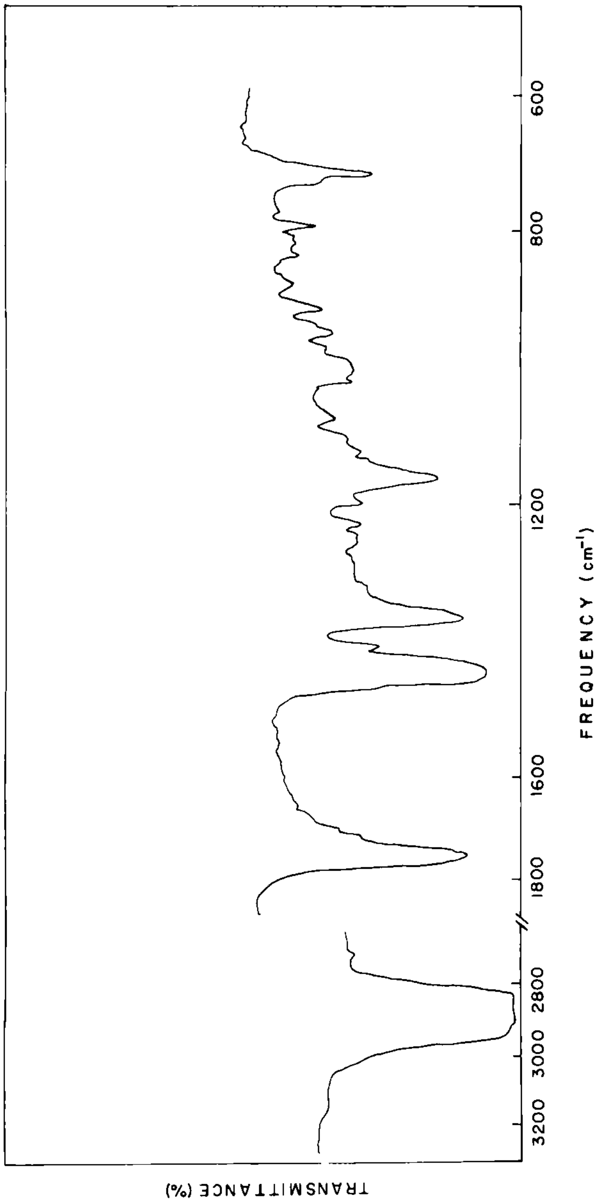

FIGURE 2 Percentage transmittance versus frequency for cholesteryl laurate.

TABLE III

Cholesteryl benzoate

Band wavelength μm	Band wave number cm^{-1}	Intensity[a]	Assignment
141.22	70.81	s	librational about the long axis
50.00	200.00	w	CH_3 torsional vibration
41.35	241.82	w	CH_3 twisting
37.41	267.32	w	CH_3 twisting
28.32	353.04	vs	CH_2 bending
24.68	405.10	m	φ—C wagging
23.33	428.56	sh	C—C deformation
22.58	442.84	s	O—C wagging
21.97	455.08	s	O—C wagging
20.94	477.52	w	C—C deformation
20.46	488.74	s	φ—C deformation
19.05	524.96	m	CH_2 rocking
18.08	553.04	s	C—C out-of-plane bending

[a] See footnote in Table VI.

TABLE IV

Cholesteryl methyl carbonate

Band wavelength μm	Band wave number cm^{-1}	Intensity[a]	Assignment
140.61	71.12	w	libration about the long axis
55.77	179.31	s	CH_3 twisting
48.74	205.15	s	CH_3 torsional vibration
34.28	291.67	m	C—C torsion
31.91	313.39	s	benzene ring rocking
25.67	389.61	s	C—C in plane bending
23.31	428.84	m	C—C deformation
22.93	436.05	w	C—C deformation
22.72	440.17	w	C—C deformation
21.90	456.65	s	O—C wagging
21.42	466.95	sh	CH_3 out-of-plane bending
20.95	477.25	s	C—C deformation
20.60	485.49	vs	φ—C deformation
17.85	560.18	m	C—C out-of-plane bending
17.53	570.38	s	C—C out-of-plane ring deformation

[a] See footnote in Table VI.

TABLE V

Cholesteryl ethyl carbonate

Band wavelength µm	Band wave number cm^{-1}	Intensity[a]	Assignment
140.61	71.12	w	libration about the long axis
49.25	203.06	m	CH_3 torsional vibration
34.76	287.72	sh	C—C torsion, CH_3 bending
29.85	335.00	sh	C—C in plane bending
24.94	401.02	s	C=O wagging
22.79	438.76	m	C—C deformation
21.88	457.12	s	O—C wagging
21.44	466.30	sh	CH_3 rocking
20.90	478.54	sh	C—C deformation
20.55	486.70	s	φ—C deformation
17.85	560.32	w	C—C stretching
17.52	570.72	s	C—C out-of-plane ring deformation

[a] See footnote in Table VI.

arrangement in the crystalline state.[18,21,22] Also, the X-ray diffraction studies on cholesteryl myristate[23] indicates that the extended side chains in mesogenic materials are purported to play a major role in the structural conformation and stabilization of cholesteric phase. In such a situation, it is conceivable that infrared absorption spectra of groups directly linked to the extended chains should show observable changes in frequency and relative intensity depending upon the lengths of the chain or the groups attached to them. We observe a shift in the carbonyl frequency for cholesteryl laurate (1680 cm^{-1}) as compared with cholesteryl benzoate (1670 cm^{-1}). This may be due to the fact that the carbonyl (C=O) group in cholesteryl laurate is attached to a very long chain as compared with cholesteryl benzoate, which affects the coplanarity with the benzene ring. The relative intensities of carbonyl (C=O), methyl and methylene stretching, methyl and methylene symmetric and asymmetric deformation vibrational bands are weak in cholesteryl laurate as compared with cholesteryl benzoate indicating the effect of extended chain in cholesteryl laurate.

An absorption peak is observed at 71 (cholesteryl methyl carbonate, cholesteryl ethyl carbonate and cholesteryl benzoate) and 78 cm^{-1} (cholesteryl laurate) in the far-infrared region. This is assigned to the libration (torsional oscillation) of the cholesteric frame work about a long axis. We observed a shift in this frequency for cholesteryl laurate (78 cm^{-1}) as compared with other compounds under consideration. This is again due to the fact that the cholesteryl laurate has a very long side chain, which affects the torsional oscillation of the cholesteryl moiety. Similar absorption bands have been observed in the rotator[24] and isotropic[25–28] phases of dipolar molecules in this region. All these

TABLE VI

Cholesteryl laurate

Band wavelength μm	Band wave number cm^{-1}	Intensity[a]	Assignment
128.85	77.61	m	libration about the long axis
34.88	286.70	m	CH_2 bending
24.75	404.08	m	C=O wagging
23.73	421.42	w	φ—C wagging
23.11	432.64	w	C—C deformation
21.78	459.16	m	O—C wagging
21.49	465.28	w	CH_3 rocking
20.81	480.58	w	C—C deformation
20.42	489.76	s	φ—C deformation
18.76	527.54	w	CH_2 rocking
18.15	551.00	m	C—C stretching

[a] vw = very weak
w = weak
m = medium
s = strong
vs = very strong
sh = shoulder

[b] δ(C—H) = C—H deformation vibration
$\delta_{sy}(CH_3)$ = CH_3 symmetric deformation vibration
$\delta_{asy}(CH_3)$ = CH_3 asymmetric deformation vibration
$\delta_{asy}(CH_2)$ = CH_2 asymmetric deformation vibration
ν(C=O) = C=O stretching
β(C—C) = C—C in-plane deformation
β(C—H) = C—H in-plane deformation
β_{ske}(C=C) = C=C skeletal in-plane deformation in benzene
$r(CH_2)$ = CH_2 rocking deformation
γ(C—H) = C—H out-of-plane deformation
$r(CH_3)$ = CH_3 rocking
ν(C—O) = C—O stretching
$\omega(CH_2)$ = CH_2 wagging
R = coupled skeletal and CH_3 in-plane rocking.

are of intermolecular origin. Experimental results and theoretical appraisals[29,30] agree that this absorption is part of the molecular rotational mode, i.e., a high frequency adjunct to the microwave (Debye) relaxation absorption.

Comparison with the previously reported results for MBBA[5] leads to the expectation that the absorption in cholesteryl compounds should occur at lower wave numbers than found in MBBA, since γ_{max} is inversely[31] proportional to the square root of the relevant component of the inertia tensor. Also, the integrated intensity per molecule of the absorption band is by Gordon's sum rule[32] proportional to the squares of the relevant dipole components and inversely to the sum of the inertia tensor components. Hence, the intensity

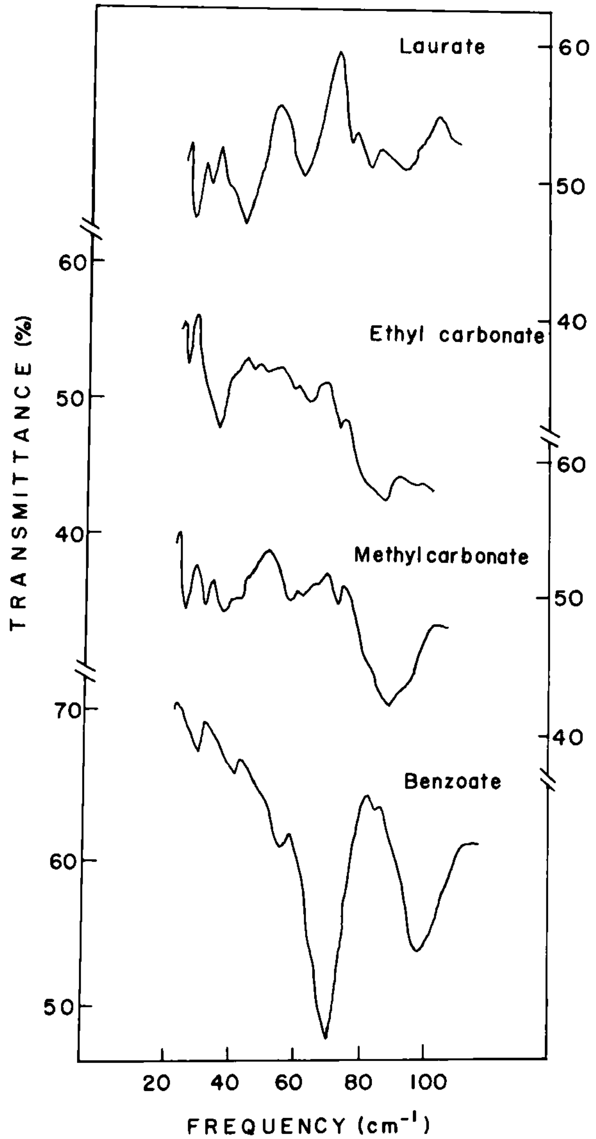

FIGURE 3 Far-infrared absorption spectra of cholesteryl benzoate, methyl and ethyl carbonates and laurate (20–100 cm^{-1}).

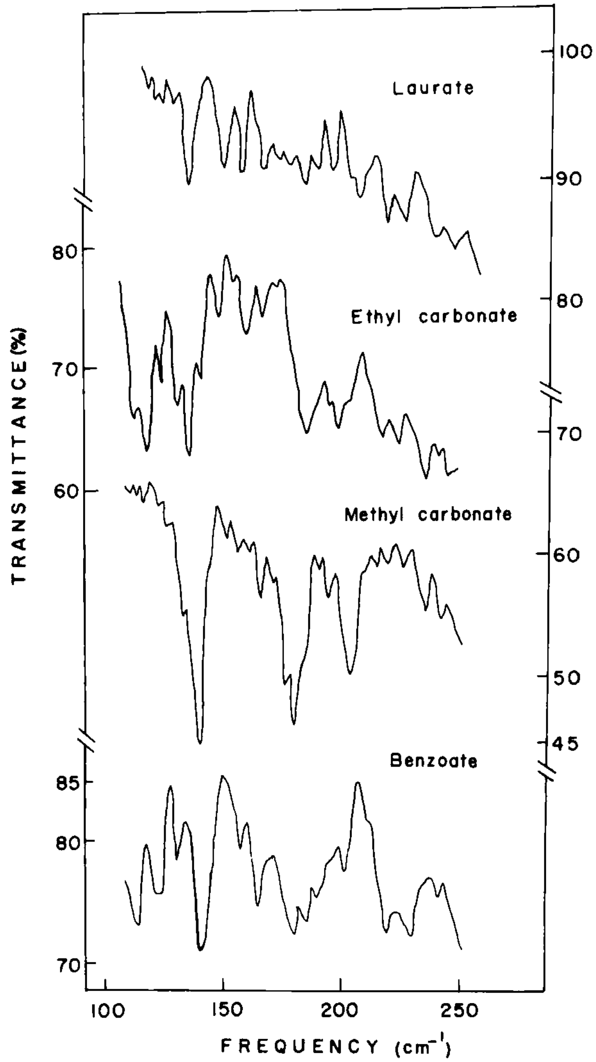

FIGURE 4 Far-infrared absorption spectra of cholesteryl benzoate, methyl and ethyl carbonates and laurate (100–250 cm^{-1}).

would be expected to be smaller in all these compounds than in MBBA since the former is heavier and has a smaller dipole moment. Both these predictions regarding the frequency of maximum absorption and the absorption intensity are experimentally confirmed.

We have observed few absorption bands at 95, 110, 138, 163, and 200 cm^{-1} (cholesteryl methyl and ethyl carbonate, and benzoate) and at 88, 131, 156, and 210 cm^{-1} (cholesteryl laurate). The bands occurring in the range 190–212 cm^{-1} probably arise from CH_3 torsional modes. The absorption centered around 110 cm^{-1} is clearly similar to FIR band observed in other liquid crystals[3,6,7,10,11] and polar liquids.[2,4] In these cases the absorption bands are thought to arise from hindered rotatory modes of the molecules, reflecting their nearest neighbor intermolecular coupling.

CONCLUSION

The infrared absorption of cholesterogenic compounds is seen to be primarily influenced by intramolecular and short range effects within a given molecular layer rather than by interactions sensitive to long range correlations within a layer or between adjacent layers.

The long side chain in the cholesterogenic materials is purported to play a major role in the structural conformation and stabilization of the cholesteric phase, confirming the results of earlier studies of the X-ray diffraction. The changes in the relative intensities and the frequency shifts of the carbonyl and librational vibration frequencies indicates the deviation from coplanarity with the skeleton of the molecule.

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