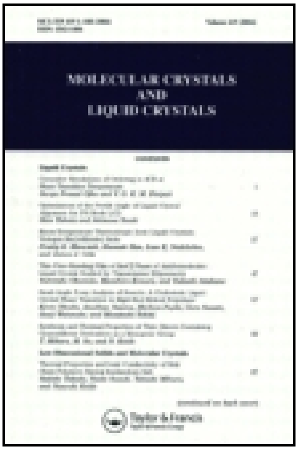

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Infrared Spectroscopic Studies of Homologous Cholesteric Liquid Crystals

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Infrared Spectroscopic Studies of Homologous Cholesteric Liquid Crystals

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Infrared (500–2500 cm^{-1}) spectra of cholesteryl alkyl carbonates (methyl, ethyl and oleyl) have been examined in the solid (cholesteryl methyl carbonate and cholesteryl ethyl carbonate) and liquid crystalline (cholesteryl oleyl carbonate) states. An attempt has been made to correlate the variation in the intensities and frequency shifts with the molecular structures. The shift in the carbonyl frequency in the case of cholesteryl oleyl carbonate may be correlated with the affect on the coplanarity with benzene ring.

1 INTRODUCTION

It is well established that the molecular structure in the crystalline state of mesogenic materials will pre-determine the ordering of the molecules in the liquid crystalline state, such as imbrication of molecules in nematic liquid crystals, macroscopic helical structure in cholesteric liquid crystals and give insight into the physical properties which are strongly dependent on molecular arrangement.[1–4] In view of this, various physical techniques such as NMR[5,6] X-ray diffraction[7–15] studies have been used to obtain information regarding molecular structure. Presently we have employed the infrared spectroscopic technique in the solid (cholesteryl methyl carbonate and cholesteryl ethyl carbonate) and liquid crystalline (cholesteryl oleyl carbonate) states and tried to correlate the observed frequency shifts and relative intensity variations with the molecular structural conformation in the crystalline state for the series of cholesteryl alkyl carbonates, which are of great biological and technological implications.

2 EXPERIMENTAL

All chemicals were purchased from Eastman Organic Chemicals Division. The samples were recrystallized before use. The spectra were obtained on a Zeiss UR 10 spectrophotometer equipped with LiF, NaCl and KBr prisms and providing a recording spectral range of 400–5000 cm^{-1}. The spectra were recorded (percentage absorbance versus wavelength) on charts of 10 cm width. The chart was self calibrated every 10 and 100 cm^{-1} with the NaCl prism, the wavenumber accuracy was ± 1.5 cm^{-1} at 700 cm^{-1} and ± 3.5 cm^{-1} at 1500 cm^{-1}. The spectra were recorded with Nujol as mulling medium between KBr plates for cholesteryl methyl carbonate and cholesteryl ethyl carbonate in the solid state. The spectrum for the cholesteryl oleyl carbonate was recorded in the liquid crystalline state at room temperature by taking the sample in between KBr plates. Tables I to III give the corrected band positions, relative intensities and assignments of the frequencies observed in the solid state for cholesteryl methyl and cholesteryl ethyl carbonate and in the liquid crystalline state for cholesteryl oleyl carbonate and the spectra are reproduced in Figures 1 to 3.

TABLE I

Cholesteryl methyl carbonate

Band wavelength (μm)	Band wavenumber cm^{-1}	Intensity[a]	Assignment[b]
4.04	2475	m	
4.54	2202	v	
4.73	2114	vw	
4.85	2060	m	Characteristic pattern of overtones and combination bands (ring structure)
5.35	1868	vw	
5.50	1818	vw	
5.58	1791	vw	
5.67	1765	vw	
5.89	1696	m	ν(C=O)
6.10	1638	vw	
6.27	1595	m	β_{ske}(C=C)
6.48	1543	vw	
6.87	1454	vw	$\delta_{asy}(CH_3)$; $\delta_{asy}(CH_2)$
7.00	1428	w	$\delta_{sy}(CH_2)$
7.25	1379	w	$\delta_{sy}(CH_3)$; Nujol
7.33	1363	sh	$\delta_{sy}(CH_3)$
7.46	1341	s	δ(C—H)
8.00	1250	vs	β(C—H)
8.04	1243	sh	$\omega(CH_2)$
8.21	1218	w	$\omega(CH_2)$
8.42	1188	m	β(C—H)
8.54	1171	m	β(C—H)
8.79	1137	m	Skeletal —CH$(CH_3)_2$

(continued)

TABLE I (*continued*)

Band wavelength (μm)	Band wavenumber cm^{-1}	Intensity[a]	Assignment[b]
9.25	1081	w	β(C—H)
9.33	1072	m	β(C—H)
9.54	1048	s	$r_y(CH_3)$
9.83	1017	s	$r(CH_3)$; β(C—H)
10.00	1000	s	β(C—C)
10.17	984	sh	R
10.33	967	m	
10.87	920	m	
11.33	882	s	γ(C—H)
11.58	863	vw	γ(C—H)
11.79	848	w	γ(C—H)
12.00	833	m	γ(C—H)
12.58	795	vs	γ(C—H)
12.79	782	vs	γ(C—H)
13.21	757	sh	γ(C—H)
13.46	743	sh	γ(C—H)
13.79	725	s	$r(CH_2)$
14.42	694	vs	γ(C—H)
14.62	684	vs	γ(C—H)
15.83	632	w	
16.67	600	w	
16.96	590	vw	
17.46	573	vs	φ(C—C)

[a] See footnote in Table III.

[b] See footnote in Table III.

TABLE II

Chhlesteryl ethyl carbonate

Band wavelength (μm)	Band wavenumber cm^{-1}	Intensity[a]	Assignments[b]
4.04	2475	m	
4.54	2202	vw	
4.83	2069	w	
5.31	1882	vw	Characteristic pattern of overtones and combination bands (ring structure)
5.56	1798	vw	
5.67	1765	vw	
5.89	1696	m	ν(C=O)
6.23	1605	m	β_{ske}(C=C)
6.46	1548	w	
7.00	1428	m	$\delta_{sy}(CH_2)$
7.21	1387	m	$\delta_{sy}(CH_3)$; Nujol
7.42	1348	m	δ(C—H)
7.96	1256	s	β(C—H)
8.21	1218	vw	$\omega(CH_2)$
8.42	1188	s	β(C—H)
8.50	1176	sh	β(C—H)
8.79	1137	s	Skeletal —$CH(CH_3)_2$

(*continued*)

TABLE II *(continued)*

Band wavelength (μm)	Band wavenumber cm^{-1}	Intensity[a]	Assignments[b]
9.25	1081	sh	β(C—H)
9.50	1053	s	$r_\gamma(CH_3)$
9.58	1043	sh	$r_\gamma(CH_3)$
9.75	1026	w	ν(C—O)
10.12	988	s	R
10.33	967	sh	
10.83	923	m	
11.08	902	m	
11.33	882	s	γ(C—H)
11.75	851	w	γ(C—H)
12.00	833	vw	γ(C—H)
12.58	795	vs	γ(C—H)
13.33	750	w	γ(C—H)
13.79	725	s	$r(CH_2)$
14.62	684	vs	γ(C—H)
15.79	633	vw	
16.67	600	vw	
17.37	575	vs	φ(C—C)

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

TABLE III

Cholesteryl oleyl carbonate

Band wavelength (μm)	Band wavenumber cm^{-1}	Intensity[a]	Assignment[b]
4.04	2475	m	
4.87	2053	w	
5.25	1905	vw	Characteristic pattern of overtones and combination bands (ring structure)
5.42	1845	vw	
5.60	1785	vw	
5.96	1678	m	ν(C=O)
6.12	1634	vw	
6.29	1590	w	β_{ske}(C=C)
7.00	1428	m	$\delta_{sy}(CH_2)$
7.25	1379	s	$\delta_{sy}(CH_3)$
8.00	1250	s	β(C—H)
8.42	1188	m	β(C—H)
8.54	1171	sh	β(C—H)
8.92	1121	w	
9.25	1081	sh	β(C—H)
9.50	1053	s	$r_\gamma(CH_3)$
9.79	1021	s	$r(CH_3)$; β(C—H)

(continued)

TABLE III (*continued*)

Band wavelength (μm)	Band wavenumber cm^{-1}	Intensity[a]	Assignment[b]
10.00	1000	s	β(C—C)
10.12	988	sh	R
10.29	972	m	CH=CH(trans)
10.67	937	vw	
10.87	920	w	
11.08	902	vw	
11.37	879	w	γ(C—H)
11.62	860	m	γ(C—H)
11.75	851	vw	γ(C—H)
12.00	833	m	γ(C—H)
12.58	795	vs	γ(C—H)
13.21	757	m	γ(C—H)
13.54	738	sh	
13.71	729	s	r(CH$_2$)
13.79	725	s	r(CH$_2$)
13.96	716	s	r(CH$_2$)
14.67	682	s	γ(C—H)
15.83	632	vw	
16.62	601	vw	
17.42	574	vs	φ(C—C)

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

[b] δ(C—H) = C—H deformation vibration.
δ_{sy}(CH$_3$) = CH$_3$ symmetric deformation vibration.
δ_{sy}(CH$_2$) = CH$_2$ symmetric deformation vibration.
δ_{asy}(CH$_3$) = CH$_3$ asymmetric deformation vibration.
δ_{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.
r$_y$(CH$_3$) = CH$_3$ out-of-plane rocking.
γ(C—H) = C—H out-of-plane deformation.
φ(C—C) = out-of-plane ring deformation.
r(CH$_3$) = CH$_3$ rocking.
ν(C—O) = C—O stretching.
ω(CH$_2$) = CH$_2$ wagging.
R = Coupled skeletel and CH$_3$ in plane rocking.

3 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 between the members of the series except for the case of the carbonyl frequency. Also we

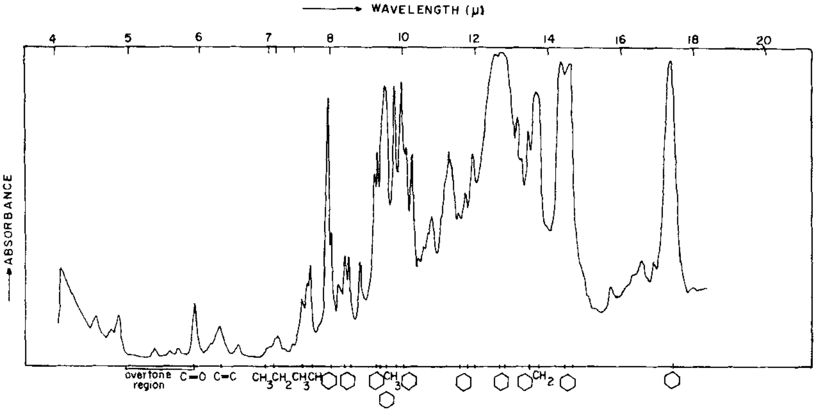

FIGURE 1 Percentage absorbance versus wavelength for cholesteryl methyl carbonate.

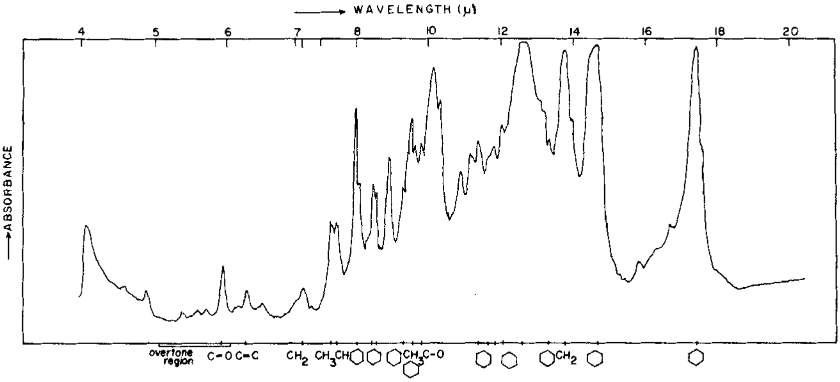

FIGURE 2 Percentage absorbance versus wavelength for cholesteryl ethyl carbonate.

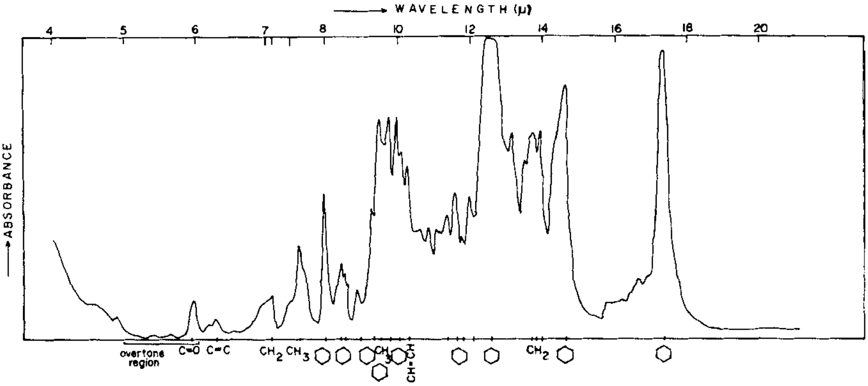

FIGURE 3 Percentage absorbance versus wavelength for cholesteryl oleyl carbonate.

do not observe much difference in the frequency assignment for cholesteryl oleyl carbonate compared to cholesteryl methyl and ethyl carbonates even though it is in the liquid crystalline state as is observed by Vergoten *et al.*[16] for nematic liquid crystals. This suggests strong dependence of the arrangement of molecules in liquid crystalline state on the previous history of molecular arrangement in the crystalline state.[17, 18] We observe a shift in the carbonyl frequency for cholesteryl oleyl carbonate (1678 cm^{-1}) as compared to cholesteryl methyl and ethyl carbonates (1696 cm^{-1}). This may be due to the fact that the carbonyl (C=O) group in cholesteryl oleyl carbonate is attached to a very long chain as compared to cholesteryl methyl and ethyl carbonates which affects the coplanarity with the benzene ring. This suggests that side chain is purported to play a major role in the structure of cholesteric phase, as is evidenced by X-ray diffraction studies on cholesteryl myristate.[11] Conjugation of the carbonyl group with an ethylenic double bond lowers the carbonyl (C=O) stretching frequency by 18 cm^{-1} in cholesteryl oleyl carbonate compared to cholesteryl methyl and ethyl carbonates. Due to vibrational coupling the observed frequency of (CH_2) groups in the case of cholesteryl oleyl carbonate splits into two components one above (729 cm^{-1}) and other below (716 cm^{-1}) a common frequency (727 cm^{-1}). This is due to the interaction of two vibrating units $(CH_2)_7$ which are separated at equal distance from the CH=CH bond which lies between two vibrating units in the cholesteryl oleyl carbonate side chain. This is not observed in the case of cholesteryl methyl and ethyl carbonates because of the lack of two vibrating units in the side chain. The relative intensity of the CH_2 rocking band is weak in the case of cholesteryl oleyl carbonate compared to methyl and ethyl carbonates. Some of the fine structure characteristics observed in the different regions of the spectra of the solid samples are found to be obliterated in the liquid crystalline phase spectra, as we notice the absence of CH_3 asymmetric and CH_2 asymmetric (1454 cm^{-1}) deformation vibrations in cholesteryl oleyl carbonate, the spectra of which is taken in the liquid crystalline phase. These two features can be explained as follows. Because of the molecular motions in the liquid crystalline phase, the intermolecular fields fluctuate rapidly, so that enduring couplings between the molecules cease to exist. Further, the increased thermal energy allows for rotations around single carbon bonds (intramolecular rotations) destroying the "all-trans" conformation of the chain. The "trans" and "gauche" links, both of which can now form, combine in all possible ways to give various "staggered" molecular configurations. The various methylenes that are in the crystalline state during any one of their coupled rocking-twisting modes of vibration and maintain specific phase relationships with one another, now become uncorrelated in phase. The modes belonging to the all-trans structure should therefore reduce the intensity in proportion to the reduction in the number of all-trans isomers. Hence in the liquid crystalline state the reduction in the intensity of CH_2 rocking (725 cm^{-1}) band is understandable. Also, we notice an additional peak at 971 cm^{-1} in cholesteryl oleyl carbonate due to the $CH{=}CH$ group which is absent from the other two members.

4 CONCLUSIONS

The long side chain in the cholesteric liquid crystalline phase is purported to play a major role in the structure of cholesteric phase, confirming the results of earlier studies on the X-ray diffraction. The changes in the relative intensities and the frequency shift of the carbonyl frequency are indicative of the deviation from coplanarity with the skeleton of the molecule.

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