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# NMR Studies of Some Cholesteric Liquid Crystalline Compounds

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# NMR Studies of Some Cholesteric Liquid Crystalline Compounds

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High resolution NMR spectra of solutions were obtained in order to find a possible explanation for the differences in transition temperatures. Only gross changes in the chemical shift of resonant lines were utilized. The experiments were done to obtain information as to the higher thermal stabilities in corresponding compounds of carboxylic esters as compared to carbonic esters. The data are not sufficient to explain the thermal stability decrease within a homologous series.

## INTRODUCTION

A number of studies of homologous series have been made to correlate mesomorphic behaviour with structural features of the molecule. Within a homologous series the transition temperatures are the result of the changes in molecular length or size and of polarizability, while for the corresponding members of different but comparable series the change of transition temperature is a measure of the chemical influence of the applied substitution.[1–3] Within a homologous series short alkyl chains favour cholesteric behaviour and longer alkyl chains give additional smectic properties; chain branching lowers the transition temperatures.[4,5] *o*- or *m*-substitution (substitutions which broaden a molecule) decreases the cholesteric–isotropic transition temperatures and *p*-substitution enhances the cholesteric–isotropic transition temperatures.[6,7] The introduction of a new double bond and the location of the substituted double bond is shown to alter the transition temperature markedly.[6,8,9] Also a decrease in the lateral attraction should manifest itself in a decrease in the smectic–cholesteric transition temperature. In this study we hoped to find experimental evidence as to the variation of mesomorphic transition temperatures due to substitutions in general. The investigation did not include complete structure analysis of each spectrum,

but compared only gross changes in the chemical shift of the resonant lines with known physical properties.

## Experimental

The spectra were obtained with a Varian-60 spectrometer operating at 60 MHz. Chemical shifts of the lines for the esters in deuterochloroform were measured at room temperature in parts per million (ppm) against tetramethylsilane (TMS) as internal standard. Solution strengths ranged from 0.3 to 0.6 molar with a sample purity of better than 99%. It was found that there were no changes in the NMR spectra for the compounds in the mesomorphic state, except for the line broadening. Visual readouts were also made from an oscilloscope before collecting the recorded data for quick checks.

## NMR spectrum

Figure 1 shows the NMR spectra of cholesteryl propionate, erucate and laurate. Figures 2 and 3 exhibit the spectra for cholesteryl methyl and ethyl carbonates, and cholesteryl oleyl carbonate and cholesteryl-2-propyn-1-yl-carbonate respectively. The sharp resonant lines that appear at 0.67, 0.82, 0.90 and 1.01 ppm arise from the methyl protons (a), (b), (c) and (d) of cholesterol[10,11] shown in Figure 4. The protons (b) will show a doublet at 0.82 and overlapping at 0.89 due to coupling with the CH proton. The methylenic protons (g) resonate around 1.13 ppm. The vinyl protons of cholesterol (f) appear as a broad doublet at 5.36 ppm.[12] Due to its coupling to the protons in ring A of cholesterol the 3α-proton (e) resonance at 4.60 ppm is theoretically composed of 27 overlapping lines. In the case of carbonic esters the 3α-proton resonance is slightly lowered. In all these esters the α-methylene group of the acyl moiety appears between 2.26 to 2.36 ppm. It will appear as a triplet in carboxylic esters and as a doublet in carbonic esters. The methylene groups of the alkyl chain could not be identified in propionate and cholesteryl methyl carbonate but for other compounds clear resonant lines appear about 1.28 ppm. This could not be identified because of the lines caused by the steroid nucleus. The absence of fine line structure and the observation of line broadening in the case of cholesteryl erucate and oleyl carbonate is due to the fact that they are liquid crystalline at room temperature.

In Table I the chemical shifts in parts per million for certain resonant lines are listed. We can see that there are not much gross changes in the chemical shift of these protons as the chain length changes. But we observe from the table that the cholesteric isotropic transition temperature decreases

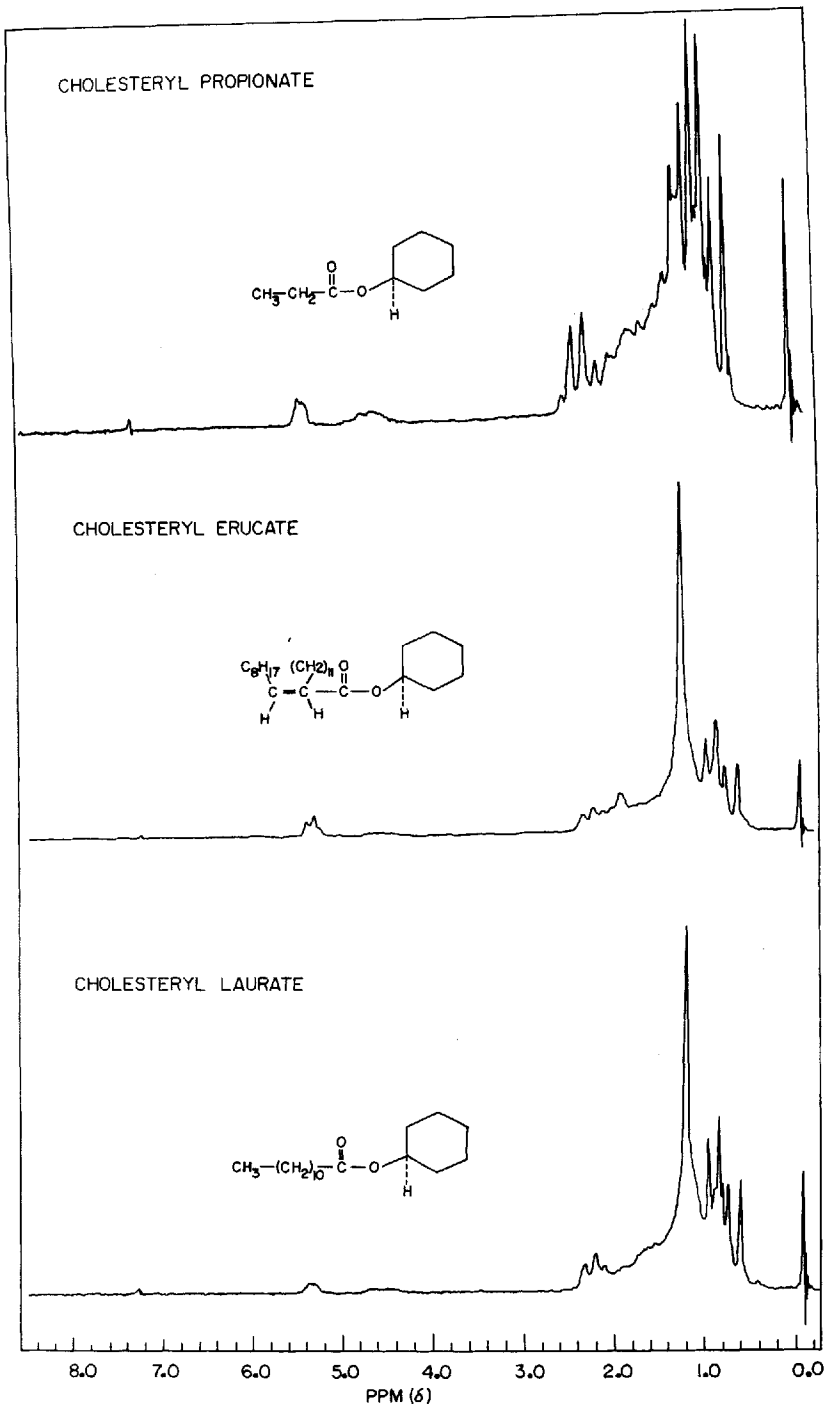


FIGURE 1 NMR spectra of cholesteryl propionate, erucate and laurate.

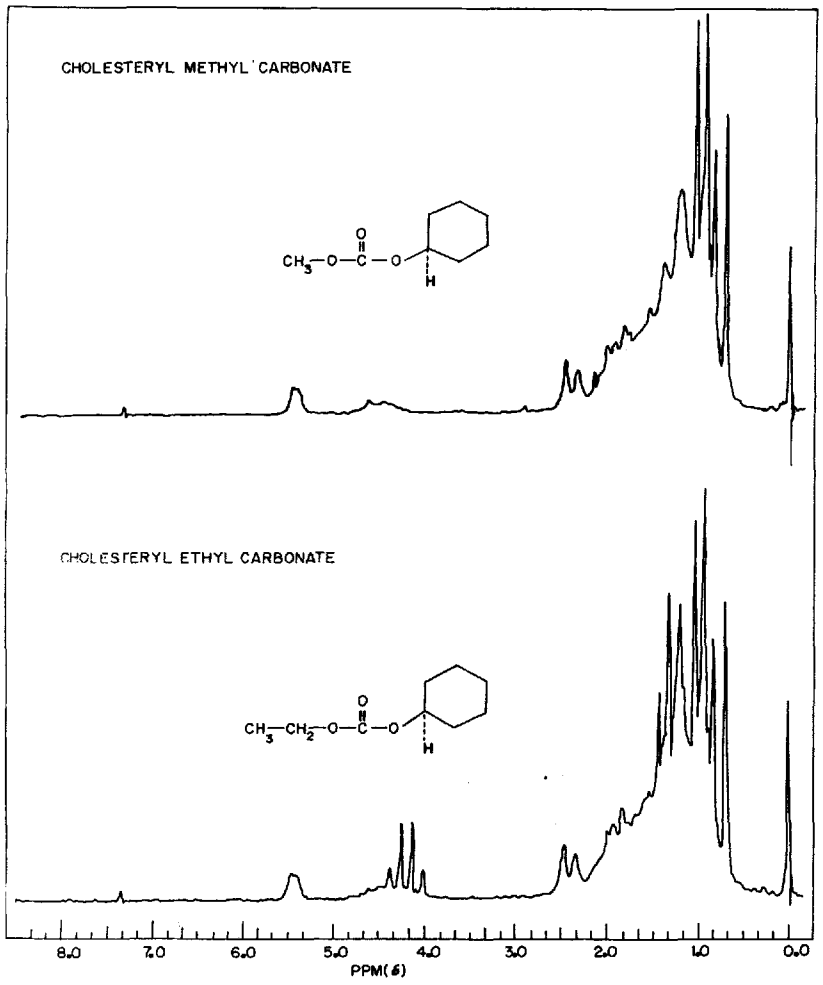


FIGURE 2 NMR spectra of cholesteryl methyl and ethyl carbonates.

as the length of the acid chain increases. There is an upfield shift of 0.1 to 0.16 ppm for the 3α-proton in carbonic esters. This indicates that the 3α-proton of the carbonic esters is more shielded than that of carboxylic esters.

## Discussion

We observe from the experimental studies that there are no major changes in any of the resonant lines as the chain length is increased in these different series of esters. But, there is an increase in the shielding of the 3α-proton as

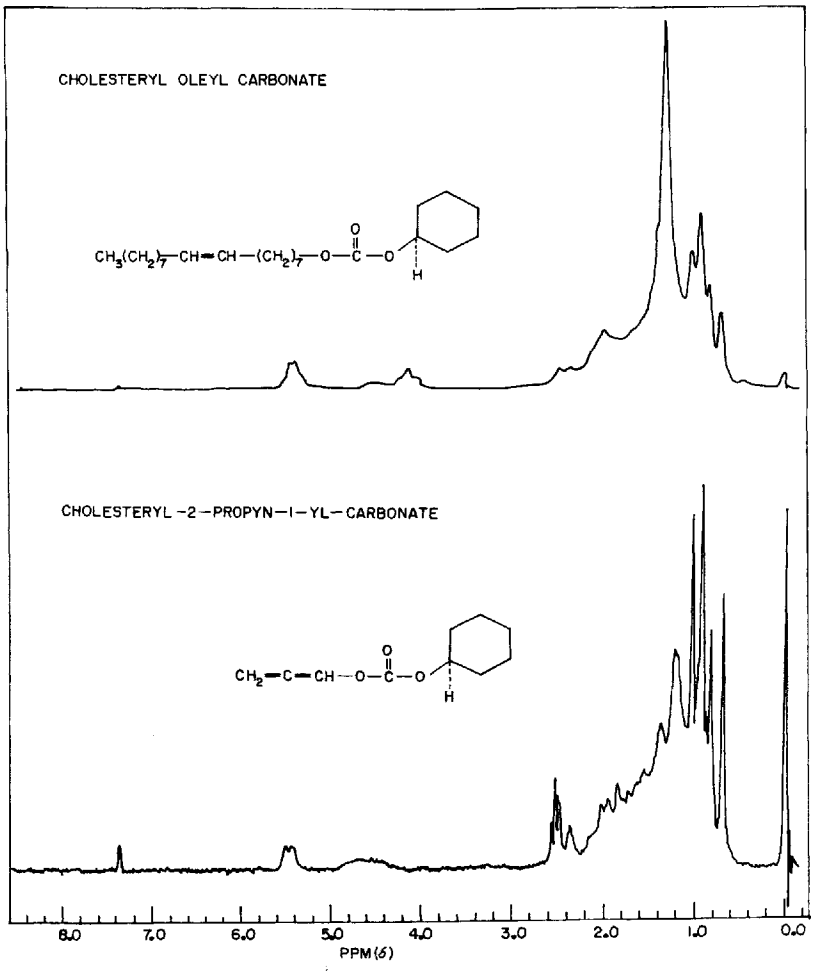


FIGURE 3 NMR spectra of cholesteryl oleyl carbonate and cholesteryl-2-propyn-1-yl-carbonate.

indicated by an upfield shift of 0.1 to 0.16 ppm for the protons in carbonic esters. Because of its electronegativity, the inductive effect of the additional oxygen existing in carbonic esters is to increase the carbonyl force constant as compared to carboxylic esters. Also the carbonyl force constant in the case of carbonic esters will be higher as compared to carboxylic esters because of the reduced overlap of the carbonyl oxygen $\pi$ electron with the carbonyl carbon $\pi$ electron due to the existence of the additional oxygen atom. This overall increase in the carbonyl force constant implies a decrease

TABLE I

List of the chemical shifts in parts per million of certain resonant lines of carbonic acid and carboxylic acid esters of cholesterol

| | Mesomorphic range in °C | Lines A | B | C | D | E | F | G | H methylene groups | I α-methylene group |
|---|---|---|---|---|---|---|---|---|---|---|
| Cholesteryl propionate | 93–95 | 0.67 | 0.82 | 0.88 | 1.01 | 4.59 | 5.37 | 1.12 | — | 2.24 |
| Cholesteryl erucate | 10–62 | 0.68 | 0.82 | 0.90 | 1.02 | 4.60 | 5.38 | — | 1.29 | 2.28 |
| Cholesteryl laurate | 89–91 | 0.68 | 0.82 | 0.89 | 1.02 | 4.61 | 5.39 | 1.13 | 1.28 | 2.29 |
| Cholesteryl methyl carbonate | 110–114 | 0.68 | 0.82 | 0.91 | 1.02 | 4.42 | 5.38 | 1.15 | — | 2.26 |
| Cholesteryl ethyl carbonate | 82–85 | 0.69 | 0.83 | 0.93 | 1.01 | 4.33 | 5.39 | 1.18 | 1.29 | 2.26 |
| Cholesteryl oleyl carbonate | 15–25 | 0.68 | 0.82 | 0.93 | 1.01 | 4.38 | 5.37 | 1.14 | 1.29 | 2.32 |
| Cholesteryl-2-propyn-1-yl carbonate | 64–94 | 0.67 | 0.81 | 0.90 | 1.01 | 4.42 | 5.38 | 1.16 | 1.27 | 2.36 |

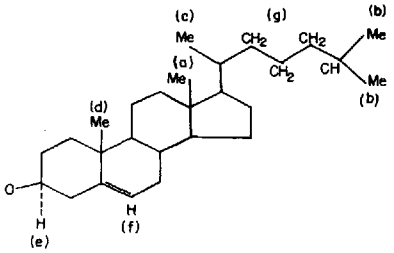


FIGURE 4 Cholesterol.

in the lateral interactions between the molecules of carbonic esters. This decrease in lateral attraction will decrease the thermal stability of the cholesteric mesophase. (Thermal stability implies the mesophase–isotropic transition temperature. Phase length is a very variable quantity and will not be considered in discussing the nematic thermal stability; see G. W. Gray, *Molecular Structure and Properties of Liquid Crystals*, p. 146.) We notice that there is a reduction in thermal stability for cholesteryl methyl and ethyl carbonates as compared to cholesteryl acetate (mesomorphic range 114–116°C) and cholesteryl propionate. In the same series of esters we notice that the cholesteric isotropic temperature falls as the chain length increases. Also the chain branching reduces the cholesteric isotropic transition temperature as in cholesteryl erucate. These could not be accounted by mere gross change studies. But this study shows how in the corresponding compounds of carbonic esters, the thermal stabilities are less as compared to those of carboxylic esters.

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