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# The Mesomorphic Behavior of S-Cholesteryl Alkyl Thiocarbonates†

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The first 20 members of the homologous S-cholesteryl alkyl thiocarbonates were prepared from cholesteryl chlorothiolcarbonate and 1-alkanols. We identified the mesophases by optical means and determined the temperatures and heats of transitions with a differential scanning calorimeter. All members of this series exhibit a cholesteric mesophase and, except for the first three members, a monotropic smectic mesophase. The temperature range between the smectic-cholesteric and the cholesteric-isotropic mesophase transitions decreases with increasing chain length. It reaches about 10° for S-cholesteryl decyl thiocarbonate and remains constant for higher homologs. S-Cholesteryl butyl thiocarbonate and its higher homologs display the visible spectrum of selectively reflected light. The temperature interval of this color band is less than 0.1° for the S-cholesteryl undecyl through heptadecyl thiocarbonate.

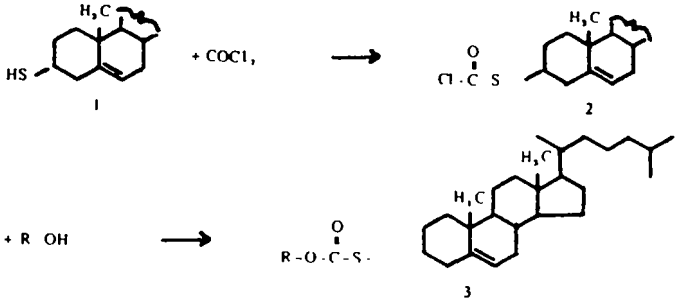
In earlier studies we observed that a sulfur atom incorporated into the functional group of the 3β-substituent of cholesteryl derivatives changes the mesomorphic characteristics.[1,2] By comparing S-cholesteryl alkanethioates[3] with cholesteryl alkanoates,[2] and cholesteryl S-alkyl thiocarbonates[4] with cholesteryl alkyl carbonates,[5] we observed that the replacement of oxygen by sulfur increases both the smectic-cholesteric and the cholesteric-isotropic transition temperatures. A similar effect occurs in azoxy compounds: diethyl azoxydibenzoate is enantiotropic smectic, while diethyl azoxydithiobenzoate exhibits a smectic mesophase with a higher transition temperature and, in addition, an enantiotropic nematic mesophase.[6,7]

† Presented at the Fourth International Liquid Crystal Conference in Kent, Ohio, August 21–25, 1972.

In this paper we will compare those outstanding features of the cholesteryl alkyl carbonates,[5] the cholesteryl S-alkyl thiocarbonates,[4] and the S-cholesteryl alkyl thiocarbonates which may be related to effects connected with replacing oxygen with sulfur. First we will describe the synthesis and pertinent mesomorphic properties of the S-cholesteryl alkyl thiocarbonates, and then discuss the experimental results of infrared and nuclear magnetic resonance spectroscopy obtained in dilute solutions. Although the molecular changes implied by the latter may not be fully applicable to the neat mesophase because of the importance of induced molecular forces, we feel that they are nevertheless meaningful.

## PREPARATION OF MATERIALS

Like all unsymmetrical carbonates, the S-cholesteryl alkyl carbonates can be obtained by a two-step reaction *via* an intermediate alkyl chloroformate. This approach was used successfully in the preparation of the stigmasteryl alkyl carbonates.[8] Because of the limited shelf life and the purification problems associated with alkyl chloroformates, this method is not very attractive. The alternate route, the reaction of cholesteryl chlorothiolcarbonate (2) with *n*-alkanols in the presence of a tertiary amine, promises a more consistent quality of the desired S-cholesteryl alkyl thiocarbonates (3):




3β-Mercaptocholest-5-ene (thiocholesterol, 1) can be phosgenated in high yield to cholesteryl chlorothiolcarbonate (2) by the slow addition of thiocholesterol and an equimolar amount of pyridine in benzene to an excess of phosgene in hexane at - 30°. The phosgene is purified and redistilled prior to use to avoid the formation of a high-melting, unidentified, side product which cannot be removed by recrystallization. The recrystallized cholesteryl chlorothiolcarbonate is then allowed to react with the respective l-alkanol in the presence of a tertiary amine. This reaction can be monitored by thin-layer chromatography, because, in contrast to cholesteryl chloroformate,[9] cholesteryl chlorothiolcarbonate is not hydrolyzed by silica gel. This observation agrees with the results of kinetic studies of the acid-catalyzed hydrolysis of thiol esters.[10]

Triethylamine, an excellent base in the preparation of cholesteryl S-alkyl thiocarbonates,[4] gave only poor yields of 3. Besides unreacted cholesteryl chlorothiolcarbonate (2), a considerable amount of thiocholesterol (1) was obtained. Our attempts to increase the yield by the use of stronger bases, such as N-methyldicyclohexylamine, 1.5-diazabicyclo[4.3.0] non-5-ene[11] or 1.5-diazabicyclo-[5.4.0]undec-5-ene,[12] were not successful. However, the weaker base pyridine resulted in reasonable yields. Side products consisted of a small amount of thiocholesterol (1), traces of dicholesteryl disulfide (originally present in commercial thiocholesterol), and also some unreacted cholesteryl chlorothiolcarbonate (2). Since recrystallization from different solvents did not eliminate the thiocholesterol, we purified the S-cholesteryl alkyl thiocarbonates by column chromatography and monitored the eluate by thin-layer chromatography. Representative $R_F$-values are listed in Table 1.

TABLE 1

$R_F$-values on Silica Gel (pre-coated plates, Merck) in the system benzene-hexane 15 : 85 (v/v)

| | |
|---|---|
| 3β-mercaptocholest-5-ene | 0.64 |
| cholesteryl chlorothiolcarbonate | 0.75 |
| dicholesteryl disulfide | 0.36 |
| S-cholesteryl methyl thiocarbonate | 0.25 |
| S-cholesteryl octyl thiocarbonate | 0.39 |
| S-cholesteryl tridecyl thiocarbonate | 0.44 |
| S-cholesteryl octadecyl thiocarbonate | 0.48 |

For reasons discussed elsewhere,[3,4,13] the chromatographed compounds are at least 99% pure. The analytical data and the yields of analytically pure compounds are listed in the Experimental Part (Table 4). The last column of Table 2 shows that this series exhibits a very strong temperature dependence of the selectively reflected light. The fact that the temperature interval of the color band did not change in four years for materials stored in the dark, indicates a degree of chemical stability not observed in either cholesteryl alkyl carbonates[5] or cholesteryl S-alkyl thiocarbonates.[4] Since the temperature coefficient of the intensity of selectively reflected monochromatic light is approximately inversely proportional to the temperature interval of the color band,[14] our measurements imply that the S-cholesteryl alkyl thiocarbonates are among the most temperature sensitive cholesteric materials.

## MESOMORPHIC PROPERTIES

Observations made during melting point determinations in the capillary gave the first indication that all members of this series, es well as the starting material

TABLE 2

Mesomorphic Properties of S-Cholesteryl Alkyl Thiocarbonates

| R | Transition Temperatures, °C | | | Transition Entropy, ΔS, cal/mole x °K | | | Visible Spectrum, °C |
|---|---|---|---|---|---|---|---|
| | Mp | S–Ch [a] | Ch–I [b] | Mp | S–Ch [a] | Ch–I [b] | |
| Methyl | 126.6 | --- | 111.3 | 22.7 | --- | 0.13 | --- |
| Ethyl | 132.2 | --- | 109.0 | 17.2 | --- | 0.14 | --- |
| Propyl | 109.2 | --- | 96.1 | 16.1 | --- | 0.11 | --- |
| Butyl | 101.7 | 35.0 [c] | 95.8 | 16.2 | --- [d] | 0.18 | (35) [f] |
| Pentyl | 96.0 | 56.0 | 90.3 | 15.8 | --- [d] | 0.23 | 56.3–56.0 |
| Hexyl | 95.3 | 65.9 | 91.6 | 17.8 | --- [d] | 0.27 | 68.5–68.0 |
| Heptyl | 92.5 | 65.6 | 83.4 | 18.9 | --- [d] | 0.23 | 64.3–64.1 |
| Octyl | 87.7 | 66.6 | 82.8 | 19.9 | 0.31 | 0.29 | 67.3–66.7 |
| Nonyl | 76.0 | 70.2 | 82.3 | 16.5 | 0.37 | 0.28 | (72) [f] |
| Decyl | 76.5 | 70.0 | 84.0 | 21.3 | 0.39 | 0.37 | 70.2–70.1 |
| Undecyl | 87.7 | 70.4 | 81.7 | 25.4 | 0.49 | 0.36 | 70.5 [e] |
| Dodecyl | 92.5 | 69.1 | 80.2 | 25.9 | 0.60 | 0.52 | 70.5 [e] |
| Tridecyl | 79.4 | 67.9 | 78.4 | 23.3 | 0.63 | 0.49 | 68.7 [e] |
| Tetradecyl | 78.5 | 67.3 | 77.6 | 29.4 | 0.59 | 0.55 | 67.8 [e] |
| Pentadecyl | 84.4 | 66.3 | 75.9 | 29.9 | 0.73 | 0.48 | 66.5 [e] |
| Hexadexyl | 82.8 | 65.3 | 75.0 | 28.1 | 0.61 | 0.56 | 65.4 [e] |
| Heptadecyl | 70.6 | 64.3 | 73.7 | 36.4 | 0.75 | 0.71 | 64.5 [e] |
| Octadecyl | 63.0 | 63.1 | 72.6 | 29.7 | 0.63 | 0.54 | 63.2–63.1 |
| Nonadecyl | 75.8 | 62.3 | 71.3 | 42.3 | 0.78 | 0.74 | 62.5–62.3 |
| Eicosyl | 70.1 | 60.4 | 70.2 | 40.3 | 0.84 | 0.80 | 60.6–60.4 |

[a] Smectic-cholesteric transition.
[b] Cholesteric-isotropic transition.
[c] Microscopic determination.
[d] Not determinable due to freezing.
[e] Width of visible spectrum smaller than 0.1 °C.
[f] Observed only on rapid cooling.

3β-mercaptocholest-5-ene and the intermediate cholesteryl chlorothiolcarbonate, are mesomorphic. Upon cooling from the isotropic melt all but the first three homologs exhibit cholesteric colors. Using a polarizing microscope under conoscopic and orthoscopic operating conditions, we studied the compounds between cover slides in a temperature-programmed hot stage (Mettler FP-2) to determine transition points and to identify mesophases. Transition temperatures and heats of transition were measured with a modified differential scanning calorimeter (Perkin-Elmer DSC-1). [15]

The starting material, 3β-mercaptocholest-5-ene, has a monotropic cholesteric mesophase with a clearing point of 53° (reported [16] 54.5°) and exhibits selectively reflected red light on quenching the isotropic melt with ice water.

The trend that sulfur substitution leads to higher transition temperatures, is also observed in the intermediate cholesteryl chlorothiolcarbonate. Cholesteryl chloroformation is monotropic cholesteric, clears at 86.0° and displays cholesteric colors only briefly when quenched with ice water. However, cholesteryl chlorothiolcarbonate is enantiotropic cholesteric, clears at a much higher temperature (131.0°) and selectively reflects in visible on the heating and cooling.

The dependence of the transition temperatures on the alkyl chain length of 3β-sterol derivatives depicted in Figure 1 is typical of homologous series exhibiting cholesteric and smectic mesophases. The melting curve generally decreases with chain length in an erratic manner, while the curves associated with transitions in the melt are comparatively smooth. The cholesteric-isotropic transitions temperatures indicate an odd-even effect to about the eleventh homolog and then fall steadily with increasing chain length. The smectic-cholesteric transition curve shows the typical steep rise to the tenth homolog. It then steadily de-

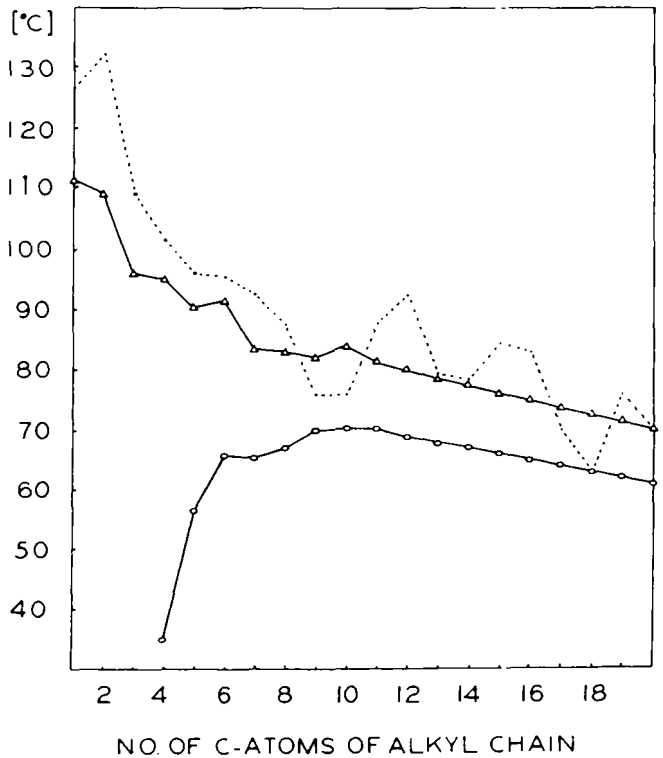



FIGURE 1 Transition Temperatures of S-Cholesteryl Alkyl Thiocarbonates: ----, melting points; -Δ-, cholesteric-isotropic transitions; -0-, smectic-cholesteric transitions.

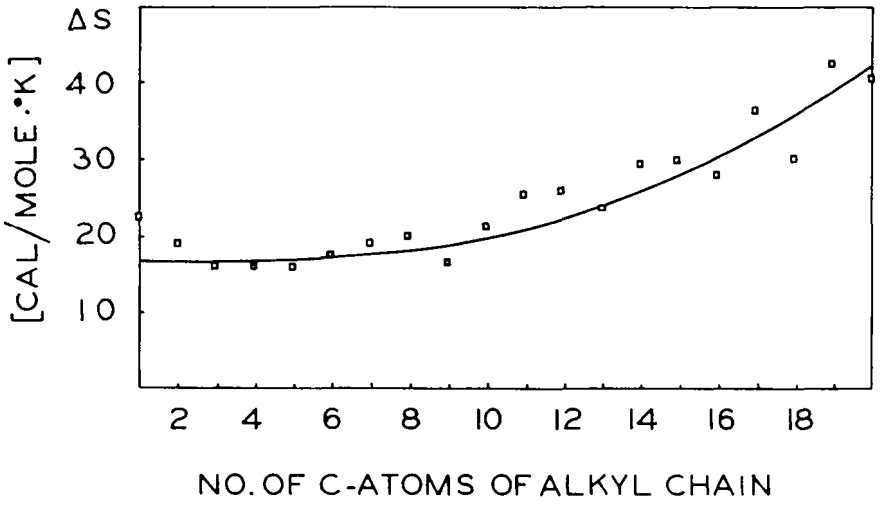



FIGURE 2 Entropy of Fusion.

creases approximately parallel to the cholesteric-isotropic transition curve. This results in a nearly constant temperature interval of about 10° for the cholesteric mesophase of the higher members. Note that the first smectic member is the S-cholesteryl butyl thiocarbonate. To our knowledge this is the lowest member of any homologous series of 3β-steryl derivatives reported to exhibit a smectic mesophase.

In Fig. 2 we plot the entropies of fusion. The values are approximately constant for the lower members but begin to increase with the tenth homolog.

The entropies of the cholesteric-isotropic and the smectic-cholesteric phase transitions, depicted in Fig. 3, are both of about the same order of magnitude and increase slightly with chain length in a very irregular manner. The deviations of the transition entropies in the melt from a smooth and simple relationship with chain length are larger than those observed in most of our homologous series containing no sulfur.[2,4,5] Since the latter were prepared and purified by essentially the same methods, the larger variations of the transition entropies may be related to the sulfur substitution. This is supported by our experience with S-cholesteryl alkanethioates[2] and S-cholesteryl ω-phenylalkanethioates.[17]

## MOLECULAR PROPERTIES

Figure 4 permits a comparison of the mesomorphic properties of the S-cholesteryl alkyl thiocarbonates and the cholesteryl S-alkyl thiocarbonates with those of

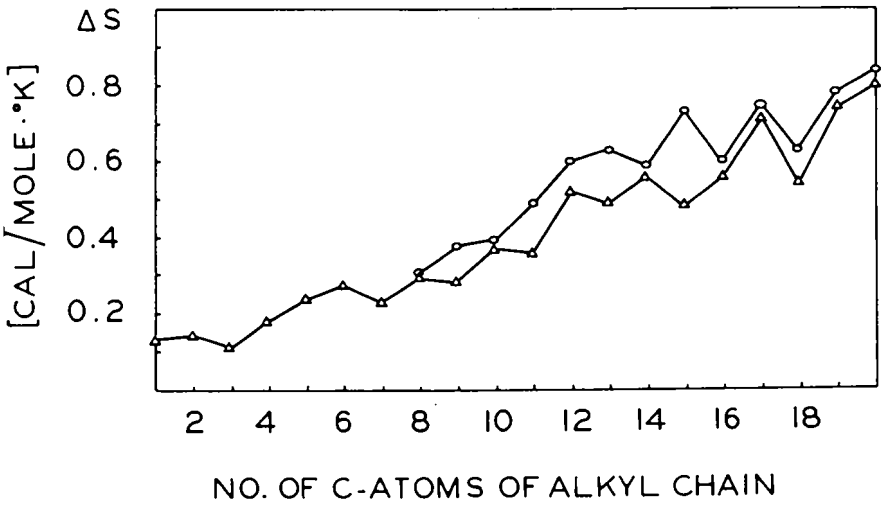



FIGURE 3 Entropies of transitions in the melt: –Δ–, cholesteric-isotropic transitions; –0–, smectic-cholesteric transitions.

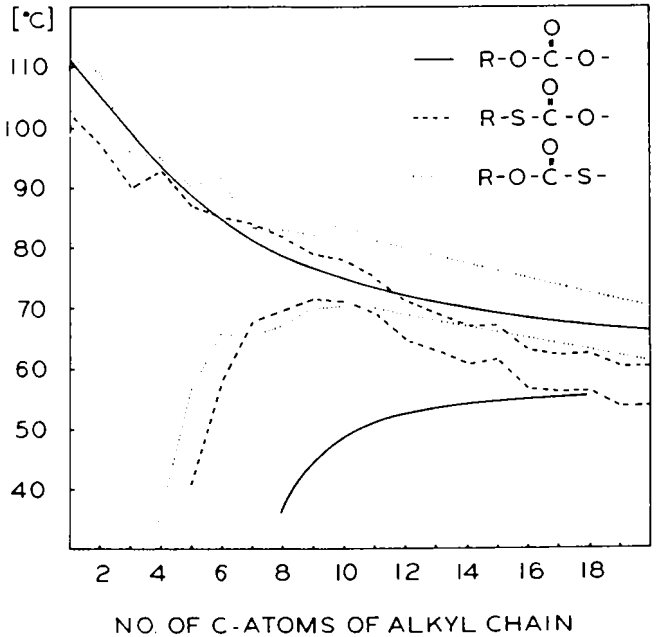
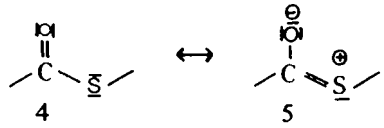



FIGURE 4 Smectic-cholesteric and cholesteric-isotropic transitions of ———, cholesteryl alkyl carbonates; – – – –, cholesteryl S-alkyl thiocarbonates; ...., S-cholesteryl alkyl thiocarbonates.

the cholesteryl alkyl carbonates. Notice that both thiocarbonate series exhibit the smectic mesophase at shorter chain lengths and at higher temperatures than the alkyl carbonates. Apparently the replacement of the carbonate group by the thiocarbonate group results in an increase of the smectic stability.

Dreiding stereo models of three corresponding analogs do not show any distinct configurational changes that can be ascribed to the substitution of oxygen by sulfur. The bulkiness of the molecules and the site of the substitution render as insignificant the fact that the bond angle of the C-O-C bond is 6° larger than that of the C-S-C bond (104°) and that the bond length of C-O is 0.4 Å shorter than that of the C-S bond (1.7 Å). Therefore, changes in the ratio of lateral to terminal attraction between the molecules must cause the differences in smectic stability.

The carbonyl group is the only common function which can be influenced by the sulfur substitution and which has a permanent polarization approximately perpendicular to the main axis of the molecule. Nyquist and Potts[18, 19] studied the difference of permanent polarization of the carbonyl group in esters and thiol esters, and in carbonates and thiocarbonates, and also the influence of inductive and mesomeric effects upon the carbonyl stretching frequency by infrared spectroscopy. They found that the inductive effect is stronger in thiol compounds due to the lower electronegativity of sulfur (O = 3.50; S= 2.60) and explained the lower carbonyl stretching frequencies observed in thiol esters with the mesomeric effect.



4 5

The greater tendency toward overlap of the carbonyl carbon $\pi$-electron with a non-bonding electron pair of the sulfur atom rather than with a non-bonding electron pair of an oxygen atom leads to the dominance of resonance structure **5** over **4**, and results in a higher polarization of the carbonyl bond in thiocarbonates. This could explain the increase of lateral attraction between molecules and therefore the higher smectic stability of the cholesteric thiocarbonates. In the following we will use IR and NMR spectroscopy to support this hypothesis.

Since we were not able to study the changes of the lateral molecular force field caused by replacing the carbonate group by the thiocarbonate group in the neat mesophase, we investigated its changes on molecules in solution. Although these experiments do not give us any information about changes of the polarization, the results should nevertheless be meaningful, because they indicate changes of the permanent polarization of the carbonyl bond. As typical representatives we arbitrarily selected the nonyl derivatives, although the results of these and previous investigations[20] indicate that the pertinent spectroscopic data do not change significantly within a homologous series.

### (a) Infrared spectroscopy

A significant change in the permanent polarization perpendicular to the main axis of the molecule, and therefore a change in the lateral attraction between molecules, can occur only at the carbonyl group, a function common to all three series. As a measure of changes in polarization and lateral moments we can therefore use the differences in the force constants, which we obtain from the infrared stretching frequencies of the carbonyl group.

Table 3 shows that the thiocarbonate sulfur lowers the C=O stretching frequency by about 30 $cm^{-1}$ regardless of whether the sulfur atom links the alkyl or the cholesteryl moiety to the carbonyl group, and independent of the matrix (KBr or Fluorolube). Nyquist and Potts[18,19] interpreted the lower carbonyl stretching frequency as proof for the dominance of resonance structure 5. The latter should also cause a corresponding difference in the stretching modes O-C-O and O-C-S. However, we were unable to assign these modes because of the complexity of the spectra below 1500 $cm^{-1}$. Considering only the carbonyl stretching modes, we find a lower force constant and therefore a greater permanent polarization of the carbonyl group in the two thiocarbonate series.

TABLE 3

Spectroscopy. (a) Chemical shift of α-emthylene protons and 3α-proton (ppm)
(b) Carbonyl stretching frequency $\nu$ ($cm^{-1}$); C–O and C–S stretching modes ($cm^{-1}$)

| | | a | | | | b | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta CH_2$ | $\Delta\delta$ | $\delta 3\alpha$ | $\Delta\delta$ | $\nu_{C=O}$ | $\Delta\nu$ | $\nu_{C-O}$ | $\nu_{C-S}$ |
| 6 | $C_8H_{17}-CH_2-S-\overset{\overset{O}{\|}}{C}-O-$ | 2.8 | | 4.6 | | 1701 | | 1168 | 625 |
| | | | −1.3 | | +0.1 | | −34 | | |
| 7 | $C_8H_{17}-CH_2-O-\overset{\overset{O}{\|}}{C}-O-$ | 4.1 | | 4.5 | | 1735 | | 1245 | --- |
| | | | +0.1 | | −1.3 | | −30 | | |
| 8 | $C_8H_{17}-CH_2-O-\overset{\overset{O}{\|}}{C}-S-$ | 4.2 | | 3.2 | | 1705 | | 1165 | 620 |

### (b) Nuclear magnetic resonance spectroscopy

The NMR study did not address the complete structure analysis of the spectra but compared only the shifts of resonant lines caused by the sulfur substitution.

The infrared spectroscopic evidence indicates an increased polarization of the carbonyl group in the thiocarbonates. Since the different electron distribution of resonance structure **5** should also affect the electron density about protons adjacent to the thiocarbonate sulfur atom, we examined the NMR spectra. The only pertinant differences noted in the complex NMR spectra of the three nonyl derivatives **6**, **7** and **8** are shifts of the resonance lines of the α-methylene protons of the alkyl moiety and of the 3α-proton. Table 3 and Figure 5 show that the signals of protons adjacent to the sulfur atom are shifted upfield by about 1.3 ppm. A similar shift of the 3α-proton resonance has recently been observed in S-cholesteryl alkanethioates.[20]

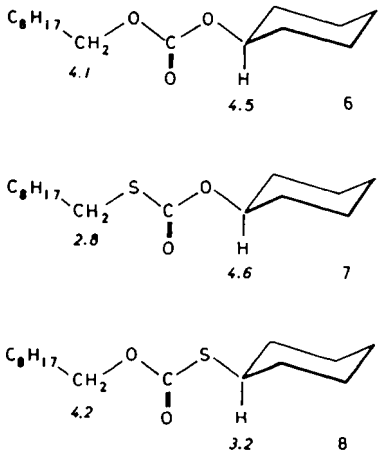



FIGURE 5 Proton resonances (ppm) in the vicinity of the carbonyl group.

This shielding effect indicates a higher electron density about protons in the vicinity of the sulfur stom, caused by the lower electronegativity of sulfur.

The signal of the 3α-proton of S-cholesteryl nonyl thiocarbonate (**8**) is shifted upfield by about the same amount (1.3 ppm) as that of the α-methylene protons of cholesteryl S-nonyl thiocarbonate (**7**). This indicates that the electron distribution is altered only between the sulfur atom and the carbonyl group. Otherwise, the chemical shifts of the 3α-proton of **7** and the α-methylene protons of **8** should be distinctly different from those of the corresponding protons of **6**, which is not observed.

## CONCLUSION

As expected from our experiments with S-cholesteryl alkanethioates,[3] the replacement of the carbonate group by the thiocarbonate group increases the smectic stability, and in addition, the chemical stability. If these S-cholesteryl alkyl thiocarbonates are stored in the dark, they are stable for several years. Furthermore, they are among the most temperature sensitive materials, because the higher members selectively reflect the light of the visible spectrum within a temperature interval of less than 0.1°.

IR and NMR spectroscopy indicate that the thiocarbonate sulfur increases the permanent polarization of the carbonyl group. This corroborates the fact that the smectic stability is increased. However, our results do not yield any information pertaining to changes of the polarizability. Only after these are known can we determine to what degree changes of the permanent polarization affect the smectic stability of the esters and carbonates of thiocholesterol.

### Acknowledgements

The authors are grateful to Mr. P.R. Boyd for his assistance in the preparation and purification of materials, and to Mr. A.J. Brown for the microscopic and calorimetric determinations.

## EXPERIMENTAL PART

### Preparation of compounds

The general procedure for the synthesis of S-cholesteryl alkyl thiocarbonates is exemplified by the preparation of S-cholesteryl ethyl and eicosyl thiocarbonates. After some experiments all thiocarbonates were prepared by the reaction of cholesteryl chlorothiolcarbonate with the respective 1-alkanol. The proportions of reactants and solvent were the same in all experiments. The reactions were run under nitrogen. The analytical data[21] and yields of analytically pure compounds are compiled in Table 4.

### Cholesteryl chlorothiolcarbonate (2)

Phosgene was passed slowly through two wash bottles containing raw linseed oil and then condensed. About 40 ml were evaporated, recondensed in the reaction flask, and dissolved in 100 ml of *n*-hexane at -30°. A solution of 100.8 g (0.25 mole) of thiocholesterol and 20 g (0.25 mole) of dry pyridine in 400 ml of absolute benzene was added slowly to the stirred phosgene solution with the temperature being maintained at -10°. After the addition, the reaction mixture

TABLE 4

S-Cholesteryl Alkyl Thiocarbonates

| R | Mp | Formula | Mol. weight | Analytical Values, % | | | | | | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Calculated | | | Found | | | |
| | | | | C | H | S | C | H | S | |
| Methyl | 126.6 | $C_{29}H_{48}O_2S$ | 460.7 | 75.59 | 10.50 | 6.96 | 75.45 | 10.60 | 7.08 | 72 |
| Ethyl | 132.2 | $C_{30}H_{50}O_2S$ | 474.8 | 75.89 | 10.62 | 6.75 | 75.81 | 10.47 | 6.50 | 82 |
| Propyl | 109.2 | $C_{31}H_{52}O_2S$ | 488.8 | 76.17 | 10.72 | 6.56 | 75.99 | 10.89 | 6.72 | 74 |
| Butyl | 101.7 | $C_{32}H_{54}O_2S$ | 502.8 | 76.43 | 10.80 | 6.37 | 76.60 | 10.93 | 6.50 | 76 |
| Pentyl | 96.0 | $C_{33}H_{56}O_2S$ | 516.8 | 76.69 | 10.90 | 6.20 | 76.76 | 10.94 | 6.40 | 73 |
| Hexyl | 95.3 | $C_{34}H_{58}O_2S$ | 530.8 | 76.93 | 11.01 | 6.04 | 77.08 | 11.07 | 5.75 | 73 |
| Heptyl | 92.5 | $C_{35}H_{60}O_2S$ | 544.8 | 77.15 | 11.10 | 5.89 | 77.24 | 11.24 | 6.10 | 76 |
| Octyl | 87.7 | $C_{36}H_{62}O_2S$ | 558.9 | 77.39 | 11.18 | 5.74 | 77.17 | 11.14 | 6.01 | 78 |
| Nonyl | 76.0 | $C_{37}H_{64}O_2S$ | 572.9 | 77.57 | 11.26 | 5.60 | 77.74 | 11.11 | 5.84 | 81 |
| Decyl | 76.5 | $C_{38}H_{66}O_2S$ | 586.9 | 77.77 | 11.33 | 5.46 | 77.68 | 11.36 | 5.52 | 65 |
| Undecyl | 87.7 | $C_{39}H_{68}O_2S$ | 600.9 | 77.94 | 11.41 | 5.34 | 77.87 | 11.53 | 5.54 | 67 |
| Dodecyl | 92.5 | $C_{40}H_{70}O_2S$ | 615.0 | 78.12 | 11.47 | 5.21 | 78.32 | 11.62 | 5.46 | 68 |
| Tridecyl | 79.4 | $C_{41}H_{72}O_2S$ | 629.0 | 78.27 | 11.53 | 5.10 | 78.32 | 11.54 | 5.25 | 65 |
| Tetradecyl | 78.5 | $C_{42}H_{74}O_2S$ | 643.0 | 78.45 | 11.60 | 4.99 | 78.39 | 11.66 | 5.14 | 66 |
| Pentadecyl | 84.4 | $C_{43}H_{76}O_2S$ | 657.1 | 78.59 | 11.65 | 4.88 | 78.45 | 11.78 | 5.10 | 64 |
| Hexadecyl | 82.8 | $C_{44}H_{78}O_2S$ | 671.1 | 78.74 | 11.72 | 4.78 | 78.82 | 11.90 | 4.91 | 64 |
| Heptadecyl | 70.6 | $C_{45}H_{80}O_2S$ | 685.2 | 78.88 | 11.77 | 4.68 | 78.71 | 11.67 | 4.68 | 65 |
| Octadecyl | 63.0 | $C_{46}H_{82}O_2S$ | 699.2 | 79.02 | 11.82 | 4.59 | 79.18 | 11.99 | 4.66 | 65 |
| Nonadecyl | 75.8 | $C_{47}H_{84}O_2S$ | 713.2 | 79.14 | 11.87 | 4.50 | 79.00 | 11.96 | 4.68 | 62 |
| Eicosyl | 70.1 | $C_{48}H_{86}O_2S$ | 727.2 | 79.27 | 11.92 | 4.41 | 79.12 | 11.92 | 4.64 | 62 |

was stirred for 2 h at 0°, overnight at room temperature, and then filtered. The filtrate was evaporated to dryness in a rotatory evaporator, and the solid residue recrystallized twice from ethyl acetate. Yield: 102.9 g (88.5%). The crystals melt (capillary) at 127.5-128.5°; the opaque melt turns green at 129.5°, blue at 131°, and clears at 133°. (Microscope: mp 128.6°; cp 133.5°).

$\nu_{max}^{KBr}$ 1758 $cm^{-1}$ (carbonyl).

Anal: Calc'd for $C_{28}H_{45}ClOS$ (465.2)
C, 72.30; H, 9.75; Cl, 7.62; S, 6.89
Found: C, 72.41; H, 10.02; Cl, 7.44; S, 7.06

**S-Cholesteryl ethyl thiocarbonate**

A solution of 1.01 g (0.01 mole) of triethylamine in 10 ml of absolute benzene was added over 30 min to a stirred solution of 4.03 g (0.01 mole) of thiocholesterol and 1.09 g (0.01 mole) of freshly distilled ethyl chloroformate in 70 ml of

absolute benzene. Stirring was continued for an additional 3 h under reflux. The cooled reaction mixture was filtered, the filtrate evaporated to dryness, the residue dissolved in *n*-hexane and chromatographed on about 250 g of silica gel (Merck: 0.06-0.2 mm). Elution with about 3,500 ml of benzene-hexane[22] 15:85 (v/v), combination of the fractions containing the thiocarbonate, evaporation of the solvent, and recrystallization of the residue twice from acetone yielded 3.90 g (82%) of colorless needles, mp 132-133°.

### S-Cholesteryl eicosyl thiocarbonate

A solution of 0.88 g (0.01 mole) of dry pyridine in 10 ml of absolute benzene was added over 30 min to a stirred solution of 4.55 g (0.01 mole) of cholesteryl chlorothiolcarbonate and 2.99 g (0.01 mole) of 1-eicosanol in 70 ml of absolute benzene. Stirring was continued for another 3 h under reflux, and the reaction mixture worked up as above. After elution with about 1,300 ml of benzene-hexane 15:85 (v/v) and recrystallization from acetone 4.5 g (62%) of fine needles were obtained; mp 69-70°.

### Purification

Since recrystallization did not completely remove some of the by-products of the reaction, the crude compounds were chromatographed on about 250 g of silica gel (Merck; 0.05-0.2 mm) and eluted with a 15:85-mixture of benzene and hexane (v/v). Cholesteryl chlorothiolcarbonate was eluted first, followed by thiocholesterol, dicholesteryl disulfide, and then the thiocarbonates. In contrast to cholesteryl chloroformate, which decomposes on silica gel-chromatography, the chlorothiolcarbonate is stable. The higher members of this series could easily be eluted, but large volumes of eluent were required for the lower members, where the separation from dicholesteryl disulfide became difficult due to close $R_f$-values. This also ruled out an increase of the benzene concentration of the eluent mixture. The eluted fractions were monitored by thin-layer chromatography for uniformity and the isolated materials were recrystallized from acetone, with a small amount of 2-butanone added for the higher members. No change in transition temperatures was observed after several additional recrystallizations. Thin-layer chromatographic analysis, including silver nitrate-impregnated silica gel, resulted in only one spot in several solvent systems. Therefore, no explanation can be given for the deviation in the smectic-cholesteric transition temperatures of the 6th, 7th, and 8th homolog from a smooth curve relationship.

### Detection of impurities

*Thin-layer chromatography*. The difficulties involved in detecting neighboring homologs within a homologous series have previously been discussed in detail[13]. In spite of the close $R_F$-values of some of the members and the by-products of the reaction (Table 1), the monitoring of the eluate from the column chromatography easily guarantees material free of starting material and side products.

### Gas-liquid chromatography of l-alkanols

Through the advent of new silicone stationary phases with a higher stability at elevated temperatures, even the higher l-alkanols can be analyzed directly. The analyses were performed on 3% OV-17, 1% OV 1, and 3% XE-61 with a Hewlett-Packard F&M Gas Chromatograph Mdl 5756 B with electronic intergrator. The alkanols used in these experiments were generally of 99.4-99.7% purity with the exception of l-tridecanol, l-pentadecanol, l-heptadecanol, and l-nonadecanol, which were only 99.0-99.2% pure. Some of the impurities could be identified as the lower homologs. Summarizing the analytical results, it can safely be stated that the purity of the homologous series of S-cholesteryl alkyl thiocarbonates is at least 99%.

### Microscopic investigation

Observations in the capillary of a melting point apparatus revealed the occurrence of a monotropic visible spectrum for all but the first three members of this homologous series. A careful investigation with a microscope in combination with a Mettler FP-2 hot stage showed the cholesteric colors to accur just above the smectic-cholesteric transition temperatures. The temperatures are corrected, but the readings are not adjusted for thermal lag due to varying heating and cooling rates. These rates were chosen to facilitate observations rather than to obtain thermal equilibrium. Therefore they vary slightly from the values obtained by differential scanning calorimetry.

### Spectroscopic data

The infrared spectra were recorded on a Beckman IR-8 spectrophotometer with the compounds examined in KBr disks and Fluorolube emulsions.

NMR spectra were obtained with a Varian HA-100 spectrometer. Chemical shifts were measured in ppm against tetramethylsilane as internal standard in deuterochloroform at room temperature. A PDP-8 computer was used to maintain system stability and to perform time avaraging functions.

## Stability

As observed in the homologous series of cholesteryl alkyl carbonates[5] and S-alkyl thiocarbonates[4] the investigated series of S-cholesteryl alkyl thiocarbonates also forms a variety of products upon exposure to light and air. Two of these products, thiocholesterol and dicholesteryl disulfide, can be identified by thin-layer chromatographic analysis. After about four years, none of the pure compounds stored in the dark showed signs of serious deterioriation.

## References


1. Elser, W., *Mol. Cryst. and Liq. Cryst.* 8, 219 (1969).
2. Ennulat, R.D., *ibid.* 8, 247 (1969).
3. Elser, W., Pohlmann, J.L.W. and Boyd, P.R., *ibid.* 11, 279 (1970).
4. Elser, W. and Ennulat, R.D., *J. Phys. Chem.* 74, 1545 (1970).
5. Elser, W., Pohlmann, J.L.W. and Boyd, P.R., *Mol. Cryst. and Liq. Cryst.* 20, 77 (1973).
6. Demus, D. and Sackmann, H., *Z. Phys. Chem.* (Leipzig) 222, 127 (1963).
7. Karg, K., Dissertation, Halle, 1934.
8. Pohlmann, J.L.W., *Mol. Cryst.* 2, 15 (1966).
9. Nakanishi, S., *Doshisha Kogaku Kaishi* 8, 80 (1957); *Chem. Abstr.* 54, 22717 (1960).
10. Janssen, M.J. in *The Chemistry of Carboxylic Acids and Esters*, S. Patai, Ed., Interscience Publ., New York, 1969, Chapt. 15.
11. Oediger, H., Kabbe, H.-J., Möller, F. and Eiter, K., *Chem. Ber.* 99, 2012 (1966).
12. Oediger, H. and Möller, F., *Angew. Chem.* 79, 53 (1967).
13. Pohlmann, J.L.W. and Elser, W., *Mol. Cryst. and Liq. Cryst.* 8, 427 (1969).
14. Ennulat, R.D., *Mol. Cryst. and Liq. Cryst.* 13, 337 (1971); see also Ennulat, R.D., Garn, L.E. and White, J.D., *ibid.* in print.
15. Ennulat, R.D. in *Analytical Calorimetry*, R.S. Porter and J.F. Johnson, Eds., Plenum Publ. Corp., New York, 1968, p. 219.
16. Leder, L.B., *J. Chem. Phys.* 55, 2649 (1971).
17. Elser, W., Pohlmann, J.L.W., and Ennulat, R.D., to be published.
18. Nyquist, R.A. and Potts, W.J., *Spectrochim. Acta* 15, 514 (1959).
19. Nyquist, R.A. and Potts, W.J., *ibid.* 17, 679 (1961).
20. Cameron, L.M., Callender, R.F. and Kramer, A.J., *Mol. Cryst. and Liq. Cryst.* 16, 75 (1972).
21. Microanalyses by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.
22. Phillips Petroleum Co., Bartlesville, OK. (This 95% *n*-hexane contains 3-methylpentane and methylcyclopentane as major contaminants).