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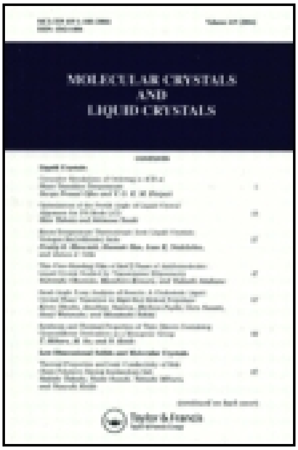

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The Mesomorphic Behavior of S-Cholesteryl ω-Phenylalkanethioates

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The Mesomorphic Behavior of S-Cholesteryl ω-Phenylalkanethioates

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(Received June 12, 1973)

The first 16 homologous S-cholesteryl ω-phenylalkanethioates were synthesized from 3β-mercaptocholest-5-ene and the imidazolides of the corresponding ω-phenylalkanoic acids. The mesomorphic properties of these compounds were determined by microscopic inspection and by differential scanning calorimetry. With the exception of the phenylthioacetate, the 4-phenylbutanethioate, and the 6-phenylhexanethioate, all homologs are cholesteric. S-Cholesteryl 8-phenyloctanethioate and its higher homologs are monotropic smectic. Both the cholesteric-isotropic and the smectic-cholesteric transition temperatures fall on two hyperbolic curves: a high temperature branch for homologs of odd and a low temperature branch for homologs of even acyl chain length. Some of the cholesteric members of this series exhibit the visible spectrum of selectively reflected light within a narrow temperature range.

In previous papers we described the odd-even effect exhibited by the homologous series of the ω-phenylalkanoates of cholesterol[1-3] and 5α-cholestan-3β-ol.[4,5] In particular we found that the cholesteric-isotropic transition temperatures fall on two distinct curves: a high temperature branch for homologs of odd and a low temperature branch for homologs of even acyl chain length. But the smectic-cholesteric transition temperatures of these two series did not exhibit this alternating effect. In a previous communication[1] on the molecular interpretation of mesomorphic behavior between different homologous series we briefly

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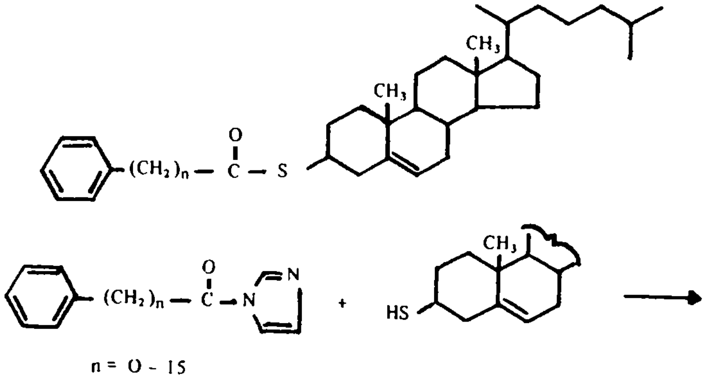
mentioned the mesomorphic properties of S-cholesteryl thiobenzoate through S-cholesteryl 8-phenyloctanethioate. We subsequently extended this series[5] to the S-cholesteryl 16-phenylhexadecanethioate and now wish to report the preparation, purification, thermodynamic, and mesomorphic properties of a homologous series of 16 S-cholesteryl ω-phenylalkanethioates.

PREPARATION

The reaction of the imidazolides of ω-phenylalkanoic acids with 3β-mercaptocholest-5-ene (thiocholesterol) under catalysis with small amounts of sodium methoxide in absolute benzene resulted in yields of 65-80% of analytically pure S-cholesteryl ω-phenylalkanethioates. Thin-layer chromatography was used to monitor the progress of the transacylation reaction. The crude reaction mixtures contained small amounts of unreacted 3β-mercaptocholest-5-ene and the side products cholesta-3,5-diene and dicholesteryl disulfide.



Since the latter could not efficiently be removed by recrystallization, we purified the crude reaction products by column chromatography on silica gel using mixtures of benzene and *n*-hexane as eluent, followed by recrystallization from acetone. The yields of analytically pure materials, the elemental analyses,[6] and the physical properties of the synthesized materials are summarized in Table 1. The transition points listed were determined microscopically with a Mettler FP-2 hot stage and the temperature readings, which agree within the limit of error with data obtained by differential scanning calorimetry, are corrected. Observations on the selective reflection of light (cholesteric colors) are recorded in the experimental part. The heats of transitions were obtained by differential scanning calorimetry.

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TABLE I

S-Cholesteryl ω-Phenylalkanethioates

		Transition Temperatures, °C			Transition Enthalpies ΔH (Kcal·mole^{-1})		
ω-phenylalkanethioate	Yield %	Mp	S-Ch(a)	Ch-I(b)	Mp	S-Ch(a)	Ch-I(b)
thiobenzoate	83	165.0	---	196.8	7.93	---	0.16
phenylthioacetate	88	125.8	---	---	6.94	---	---
3-phenylpropanethioate	75	136.3	---	145.6	8.35	---	0.096
4-phenylbutanethioate	78	98.2	---	---	8.46	---	---
5-phenylpentanethioate	78	106.5(d)	---	109.3	7.96	---	0.12
6-phenylhexanethioate	79	82.5	---	---	7.08	---	---
7-phenylheptanethioate	78	95.8	---	92.4	7.49	---	0.13
8-phenyloctanethioate	76	70.0	34.2	36.3	7.63	---	0.14
9-phenylnonanethioate	75	83.5	46.9	83.6	9.80	---	0.16
10-phenyldecanethioate	74	52.0	39.8	42.7	7.27	---	0.16
11-phenylundecanethioate	75	68.8	47.8	76.3	7.29	---	0.17
12-phenyldodecanethioate	72	45.8	43.4	48.3	7.57	0.18	0.066
13-phenyltridecanethioate	72	67.8	48.7	71.6	10.50	---	0.21
14-phenyltetradecanethioate	68	51.0	47.3	52.8	8.04	0.23	0.082
15-phenylpentadecanethioate	66	61.1	51.1	68.8	12.80	0.15	0.22
16-phenylhexadecanethioate	65	54.6	49.4	55.3	9.01	0.24	0.116

(a) Smectic - cholesteric transition; (b) cholesteric - isotropic transition;

(c) Could not be determines due to a very slow transition or due to crystallization of sample; (d) Solid-solid transition at 97.5°.

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TABLE I (*Continued*)

S-Cholesteryl ω-Phenylalkanethioates

	Transition Entropies, ΔS (cal × mole^{-1}·°K^{-1})		Formula	Mol. Wt.	Analytical Values, %					
					Calculated			Found		
Mp	S–Ch$^{(a)}$	CH-I$^{(b)}$			C	H	S	C	H	S
18.0	---	0.33	$C_{34}H_{50}OS$	506.8	80.57	9.94	6.33	80.67	10.04	6.43
17.4	---	---	$C_{35}H_{52}OS$	520.9	80.71	10.06	6.16	80.89	10.00	6.24
20.7	---	0.21	$C_{36}H_{54}OS$	534.9	80.84	10.18	5.99	80.75	10.17	6.15
22.8	---	---	$C_{37}H_{56}OS$	548.9	80.96	10.28	5.84	80.90	10.51	5.94
21.6	---	0.31	$C_{38}H_{58}OS$	562.9	81.08	10.38	5.70	80.95	10.21	5.62
20.0	---	---	$C_{39}H_{60}OS$	577.0	81.19	10.48	5.56	81.11	10.62	5.62
20.3	---	0.35	$C_{40}H_{62}OS$	591.0	81.29	10.57	5.42	81.22	10.60	5.61
22.2	--$^{(c)}$	0.46	$C_{41}H_{64}OS$	605.0	81.39	10.62	5.30	81.56	10.79	5.37
27.6	--$^{(c)}$	0.46	$C_{42}H_{66}OS$	619.1	81.52	10.67	5.18	81.57	10.58	5.28
22.4	--$^{(c)}$	0.51	$C_{43}H_{68}OS$	633.1	81.65	10.75	5.07	81.55	10.84	5.13
21.4	--$^{(c)}$	0.48	$C_{44}H_{70}OS$	647.1	81.74	10.83	4.96	81.81	10.85	4.94
23.8	0.56	0.21	$C_{45}H_{72}OS$	661.1	81.82	10.90	4.85	81.94	10.96	4.74
30.9	--$^{(c)}$	0.62	$C_{46}H_{74}OS$	675.2	81.90	10.97	4.75	81.85	11.09	4.79
24.9	0.73	0.24	$C_{47}H_{76}OS$	689.2	81.98	11.04	4.66	82.01	11.09	4.59
38.4	0.48	0.66	$C_{48}H_{78}OS$	703.2	82.06	11.10	4.56	81.98	11.23	4.72
27.6	0.76	0.34	$C_{49}H_{80}OS$	717.2	82.13	11.16	4.47	82.07	11.32	4.58

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MESOMORPHIC PROPERTIES

The results of optical microscopy are depicted in Figure 1.

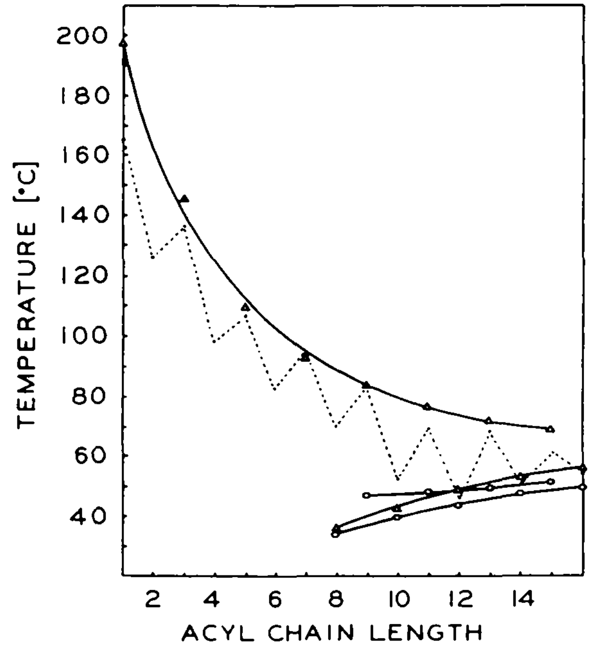

FIGURE 1: Transition Temperatures of S-Cholesteryl ω-Phenylalkanethioates - - -, melting points; ——Δ——, cholesteric-isotropic transitions; ——0——, smectic-cholesteric transitions.

The *melting points* decrease with increasing acyl chain length in an alternating manner. *Cholesteric-isotropic phase transitions* – All homologs, except S-cholesteryl phenylthioacetate, 4-phenylbutanethioate, and 6-phenylhexanethioate, are cholesteric. The odd homologs, S-cholesteryl 7-phenylheptanethioate through 15-phenylpentadecanethioate, and the even homologs 14-phenyltetradecanethioate and 16-phenylhexadecanethioate, exhibit the visible spectrum of selectively reflected light (see experimental part). S-Cholesteryl 14-phenyltetradecanethioate has an extremely narrow temperature range of the visible spectrum and is the most temperature sensitive cholesteric material which we found in our studies. We measured[7] a maximum temperature coefficient of the selective reflectance of about 50,000% per °C and a minimum detectable temperature variation of 2×10^{-5} °C at 5400 Å. The temperature interval is about 0.07° (4000-7000 Å). The temperatures of the cholesteric-isotropic phase transitions fall on two curves. The upper branch of higher transition temperatures is formed by the

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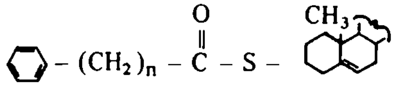
homologs of odd and the lower branch by the homologs of even acyl chain length. As in the cases of the ω-phenylalkanoates of cholesterol[1-3] and 5α-cholestan-3β-ol,[4,5] the cholesteric-isotropic transition curves of the S-cholesteryl ω-phenylalkanethioates can be curve fitted to hyperbolas, as demonstrated in Figure 1. Mathematically the two curves can be expressed as follows:

$$T_c = \frac{A}{(n+1) + n_o} + B$$



	Upper curve	Lower curve
A	636.82	-1,422.17
B	30.58	107.04
n_o	2.80	12.10
SEE*	2.63	0.53

* Standard Error of Estimate

$$SEE = \sqrt{\frac{\Sigma\,(T_{exp} - T_{calc})^2}{N}}$$

On extrapolation, the two curves intersect at about n = 19.

Smetic-cholesteric phase transitions – The first smectic member is the 8-phenyloctanethioate. The odd-even effect continues into the smectic state, although it is less pronounced. The upper branch of higher transition temperatures is formed by the homologs of odd and the lower branch by the homologs of even acyl chain length, in analogy to the cholesteric-isotropic phase transitions. The two branches can be closely curve fitted to hyperbolas:

$$T_c = \frac{A}{(n+1) + n_o} + B$$

	Upper curve	Lower curve
A	-39.17	-1,029.60
B	42.94	90.20
n_o	19.80	10.00
SEE	0.26	0.90

Entropies of Transitions – Although the melting points exhibit a pronounced alternating effect throughout the series, and odd-even effect of the associated entropies of fusion is observed only in the last five homologs.

In both the homologous series of cholesteryl ω-phenylalkanoates[1,2] and 5α-cholestan-3β-yl ω-phenylalkanoates[4] we observed two distinct branches of the cholesteric-isotropic transition entropies, a higher for the members of odd and a lower for the members of even acyl chain length. The entropies of the cholesteric-isotropic phase transitions of all the odd and the last three even S-cholesteryl ω-phenylalkanethioates exhibit a similar relationship but the entropies of the 8-phenyloctanethioate and of the 10-phenyldecanethioate are substantially higher, as a matter of fact, greater than those of their adjacent odd homologs.

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While we are at present unable to explain this discontinuity in the entropy curve of the even homologs, we would like to point out that the temperature interval of the cholesteric mesophase is only 2.1° in the 8th and 2.9° in the tenth homolog, and that neither one displays cholesteric colors. In the 12-phenyldodecanethioate, with a cholesteric range of 4.9°, a faint color could be induced by the addition of a small amount of 3β-chlorocholest-5-ene, but due to the fast cooling rate necessary, no accurate temperature reading could be obtained. With a temperature interval of the cholesteric mesophase of 5.5° in the 14-phenyltetradecanethioate, a very narrow (0.07°) cholesteric color band is observed.

An alternating effect in the entropies of the cholesteric-smectic phase transitions is indicated but could not be clearly established. Optical investigations demonstrate that the compounds can be undercooled considerably, but also revealed the high viscosity of the samples. The latter might impede the cholesteric-smectic phase transition and would explain the inability to obtain a distinct enthalpy curve on differential scanning calorimetry.

DISCUSSION

The presence of the ω-phenyl group in the 3β-acyl chain results in a pronounced alternating effect of the melting points, the cholesteric-isotropic and the smectic-cholesteric phase transition temperatures. All these odd-even effects are in phase, *i.e.*, the temperatures of the various transitions are higher for the homologs of odd than for the adjacent homologs of even acyl chain length. Because the alternating effect is much greater for the cholesteric-isotropic than for the smectic-cholesteric transitions, we obtain a rather narrow cholesteric mesophase in the homologs of even acyl chain length. It ranges from 2.1° in the 8-phenyloctanethioate to 5.9° in the 16-phenylhexadecanethioate.

A comparison with the series of S-cholesteryl alkanethioates[8] shows that the ω-phenyl group also results in much higher cholesteric-isotropic transition temperatures for the homologs of short acyl chain length, but in lower smectic-cholesteric transition temperatures.

The cholesteric-isotropic transition temperatures of cholesteryl ω-phenylalkanoates alternate with increasing acyl chain length, but the smectic-cholesteric phase transitions increase almost linearly.[1-3] The alternation of the smectic-cholesteric phase transitions of the S-cholesteryl ω-phenylalkanethioates could therefore be related to the thiol ester group. The replacement of the ester by the thiol ester group results in higher cholesteric-isotropic transition temperatures of members of odd and lower transition temperatures in members of even acyl chain length. The influence on smectic-cholesteric transition temperatures is less pronounced, but the smectic mesophase is observed at shorter chain lengths. The thiol ester group obviously leads to an increased smectic stability, as it was

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observed in S-cholesteryl alkanethioates,[8] cholesteryl S-alkyl thiocarbonates,[9] and S-cholesteryl alkyl thiocarbonates.[10]

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EXPERIMENTS

(a) Preparation of compounds

The reaction of 3β-mercaptocholest-5-ene with the imidazolides of the corresponding ω-phenylalkanoic acids in absolute benzene afforded S-cholesteryl ω-phenylalkanethioates in yields of 65-80%. Without the catalysis of sodium methoxide the yields were appreciably lower. The reactions were performed under nitrogen to prevent the oxidation of 3β-mercaptocholist-5-ene to dicholesteryl disulfide, and the course of the transacylations was monitored by thin-layer chromatography. The preparation and purification of the ω-phenylalkanoic acids[3] and of 3β-mercaptocholest-5-ene[8] have been discussed previously. The preparation of S-cholesteryl 9-phenylnonanethioate is given as a typical procedure: *S-Cholesteryl 9-phenylnonanethioate:* To a solution of 2.39 g (10 mmol) of 9-phenylnonanoic acid in 75 ml of absolute benzene, 1.78 g (11 mmol) of 1,1'-carbonyldiimidazole was added which dissolved almost completely with the evolution of CO_2. The last traces were reacted by gentle warming. After cooling, 4.03g (10 mmol) of 3β-mercaptocholest-5-ene was added, the reaction mixture stirred for 30 min at room temperature, and another 3 hr under reflux, with about 50 mg of sodium methoxide added after 1 hr. The solvent was evaporated, the residue triturated with benzene-hexane (1:9), and the precipitated imidazole filtered off. The filtrate was chromatographed on silica gel (45x300 mm; silica gel, Merck, 0.05-0.2 mm) using benzene-hexane (15:85) as eluent. Unreacted 3β-mercaptocholest-5-ene and cholesta-3,5-diene were eluted first, followed by dicholesteryl disulfide, and the 9-phenylnonanethioate. The fractions containing the pure compound were combined, the solvent evaporated, and the residue recrystallized from acetone. Yield: 4.45 g (75%); mp 83.5°.

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(b) Purity

Thin-layer chromatographic analysis revealed two minor side products from the transacylation reaction besides unreacted 3β-mercaptocholest-5-ene. They were identified as cholesta-3,5-diene and dicholesteryl disulfide. All three contaminants could easily be removed by column chromatography on silica gel using a benzene-hexane mixture as eluent. No other impurities could be detected by thin-layer chromatography in various solvent systems in two dimensions and on silver nitrate-impregnated silica gel. Using criteria established in our investigations of S-cholesteryl alkanethioates for the purity of 3β-mercaptocholest-5-ene[8] and the gas chromatographic analyses of the methyl ω-phenylalkanoates, we can assume a minimum purity of 99% for the synthesized S-cholesteryl ω-phenylalkanethioates.

(c) Stability

The S-cholesteryl ω-phenylalkanethioates are stable for a period of several years if they are protected from light. They are also stable on temperature-cycling through the range of the visible spectrum. A sample of the 14-phenyltetradecanethioate did not change its wavelength of maximum reflection as a function of temperature over a period of nine days and retained the temperature interval of 0.06° for the color band between 4000 and 7000 Å.[7]

(d) Spectroscopy

The IR spectra were obtained from samples examined in KBr disks, the NMR spectra from solutions in deuterochloroform with tetramethylsilane as internal standard. As expected, no gross changes in the spectra with relation to increasing acyl chain length were observed. The major stretching frequencies and resonant lines, and their comparison with those of the corresponding alkanoates and alkanethioates are listed in Table 2.

1) *Infrared Spectra:* Some of the infrared absorptions, such as the C=C in-plane vibrations of the aromatic ring at 1603 cm^{-1} and 1495 cm^{-1}, the C-H out-of-plane vibrations of the monosubstituted benzene ring at 745 cm^{-1} and 698 cm^{-1}, and the $(CH_2)_4$ vibration at 721 cm^{-1}, are identical with the respective vibrations observed in cholesteryl ω-phenylalkanoates. The shift of the C=O stretching frequency from 1726 cm^{-1} in ω-phenylalkanoates to 1675 cm^{-1} in ω-phenylalkanethioates indicates a lower force constant and therefore a greater permanent polarization of the carbonyl group in ω-phenylalkanethioates.

2) *Nuclear Magnetic Resonance Spectra:* This investigation does not include a complete analysis of each spectrum but compares only gross changes in the chemical shifts of the resonant lines. The spectra consist of a 5H multiplet at

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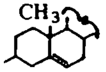
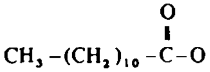
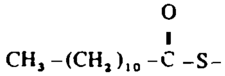
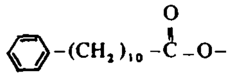
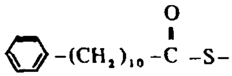
TABLE II

Spectroscopic comparison of alkanoates and ω-phenylalkanoates with corresponding alkanethioates and ω-phenylalkanethioates of cholesterol. a) infrared (cm^{-1}); b) NMR (ppm) data

	a			b		
 CH_3	$\nu_{C=O}$	ν_{C-O}	δM,5H phenyl ring	δT,2H α-CH_2	δM,1H 3α-H	δD,1H 6-H
 $CH_3-(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-O$	1725	1170	-	2.26	4.60	5.36
 $CH_3-(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-S-$	1678	-	-	2.50	3.33	5.38
 $-(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-O-$	1726	1170	7.18	2.24	4.56	5.36
 $-(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-S-$	1675	-	7.18	2.45	3.25	5.36

7.18 ppm (benzenoid protons), a 2H triplet at 2.45 ppm (α-methylene group protons of the acyl chain), a very broad 1H multiplet at 3.25 ppm (3α-proton), and a broad 1H doublet at 5.36 ppm (6-proton). The 3α-protons of the phenylthioacetate resonate at 3.76 ppm (*versus* 3.61 ppm in the phenylacetate). A comparison of the chemical shifts between the ω-phenylalkanoates and ω-phenylalkanethioates shows an upfield shift of about 1.32 ppm for the 3α-proton and a 0.21 ppm downfield shift for the 3α-methylene protons of the acyl side chain of the ω-phenylalkanethioates. Similar shifts of about the same orders of magnitude have previously been reported for cholesteryl alkanoates and S-cholesteryl alkanethioates,[11] as well as cholesteryl alkyl carbonates and thiocarbonates.[10] The greater shielding of the 3α-proton in the S-cholesteryl ω-phenylalkanethioates supports the decrease in the force constant of the carbonyl group as observed in the C=O stretching frequency. These data, neglecting any changes in polarizability in the neat mesophase, imply an increase of lateral attraction between molecules, and could explain the greater smectic stability of S-cholesteryl ω-phenylalkanethioates.

(e) Cholesteric properties

The visible spectrum of selectively reflected light was determined on a temperature controlled Mettler FP-2 hot stage under the microscope. The temperature values were obtained on cooling and the readings are corrected. The first homolog of odd chain length to exhibit cholesteric colors is the 7-phenylheptanethioate, the first homolog of even acyl chain length the 14-phenyltetradecanethioate. In spite of excessive undercooling and quenching of the isotropic melt in ice water, no cholesteric colors could be observed in the 8-phenyloctanethioate, the 10-phenyldecanethioate, and the 12-phenyldodecanethioate.

S-Cholesteryl 7-phenylheptanethioate: The focal-conic texture appears at 91.9°, changing to blue at 43.5°, to green at 40.8°, to yellow at 39.4°, to orange at 36.6° and to red at 33.8° with crystallization.

S-Cholesteryl 9-phenylnonanethioate: 50.3° violet, 49.8° blue, 49.5° green, 49.2° yellow, 48.8° orange, 48.7° red, 48.1° color gone.

S-Cholesteryl 11-phenylundecanethioate: 49.9° violet, 49.6° blue, 49.3° green, 49.1° yellow, 48.9° orange, 48.7° red, 47.8° disappeared.

S-Cholesteryl 13-phenyltridecanethioate: 51.1° violet, 50.7° blue, 50.4° green, 50.2° yellow, 50.1° orange, 50.0° red, and 49.8° disappeared.

S-Cholesteryl 14-phenyltetradecanethioate exhibits an extremely narrow color band around 47.35°.

S-Cholesteryl 15-phenylpentadecanethioate: 52.5° violet, 52.4° blue, 52.2° green, 52.1° yellow, 51.9° red which disappears at 51.3°.

S-Cholesteryl 16-phenylhexadecanethioate: 49.6° violet, 49.55° blue and green, 49.5° red and disappearing at 49.45°. The temperature interval of the visible spectrum is about 0.15°.

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