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Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

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Wolfgang Elser [a]

[a] U.S. Army Electronics Command, Night Vision Laboratory, Fort Belvoir, Virginia

Version of record first published: 28 Mar 2007.

To cite this article: Wolfgang Elser (1966): The Mesomorphic Behavior of Cholesteryl n-Alkyl Carbonates, Molecular Crystals, 2:1-2, 1-13

To link to this article: http://dx.doi.org/10.1080/15421406608083055

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Molecular Crystals. 1966. Vol. 2, p.p 1–13
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The Mesomorphic Behavior of Cholesteryl n-Alkyl Carbonates

WOLFGANG ELSER

U.S. Army Electronics Command, Night Vision Laboratory, Fort Belvoir, Virginia

Received December 9, 1965

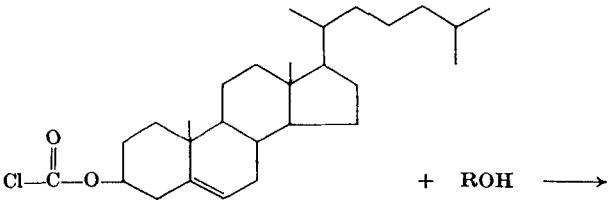
Abstract—A homologous series of cholesteryl n-alkyl carbonates has been prepared and their mesophases investigated. Different groups can be distinguished depending on the length of the alkyl chain. The first two members exhibit a monotropic high-temperature color band, the next two members an enantiotropic high-temperature color band, followed by a monotropic low-temperature color band without an interruption in the color sequence; the following five members an enantiotropic high-temperature and a clearly separated low-temperature color band, and the last four members a monotropic high-temperature and a separated monotropic low-temperature color band. The mechanical sensitive enantiotropic high-temperature color band could only be observed in reflection under the microscope. The monotropic low-temperature color band, which is essentially induced by disturbance, was found in both reflection and transmission, with the colors of the same intensity.

A program in this laboratory is concerned with the synthesis and structural characterization of mesomorphic compounds of the cholesteric type. The cholesteric mesophase[1] is mainly formed by suitable derivatives of cholesterol, e.g., cholesteryl esters derived from open-chain aliphatic acids,[2] and the mesophase derives its name from this fact. The first four mesomorphic members of cholesteryl alkyl carbonates were described by Däumer.[3] On cooling of the isotropic liquid he observed a birefringent phase, which, on slight pressure, oriented itself and showed a negative optical sign. All four members, cholesteryl methyl through butyl carbonate, were reported as enantiotropic, with the methyl carbonate having a second solid state.[3, 4, 5] It was of interest to prepare higher members of this series, to see if additional phases could be

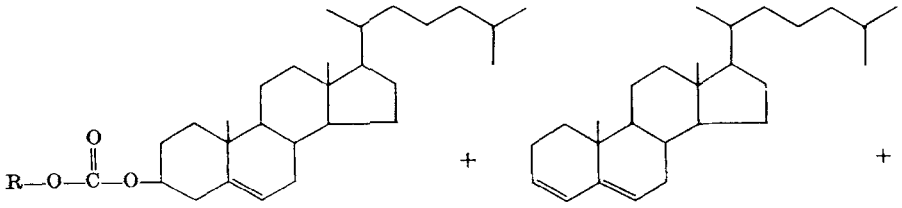
found with increasing chain length as in the case of cholesteryl alkyl esters.[2]

I. Preparation

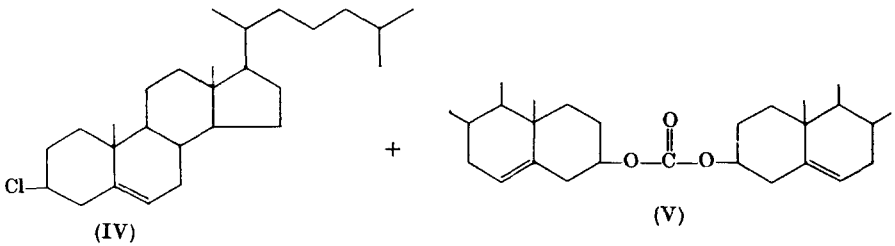
(a) Cholesteryl chloroformate[6] (I) and alkanols, in the presence of pyridine, form the corresponding cholesteryl alkyl carbonates (II), with minute amounts of cholesta-3,5-diene (III),



(I)



(II) (III)



(IV) (V)

3β-chloro-cholest-5-ene (IV), and, in some cases, di-cholesteryl carbonate (V), as judged by thin-layer chromatography. All these side products are also obtained when an excess of pyridine reacts with cholesteryl chloroformate in boiling benzene.

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(b) The reaction of cholesterol (VI) with the corresponding alkyl chloroformate, under essentially the same conditions, leads to a product containing only traces of di-cholesteryl carbonate (V) together with some unreacted cholesterol.

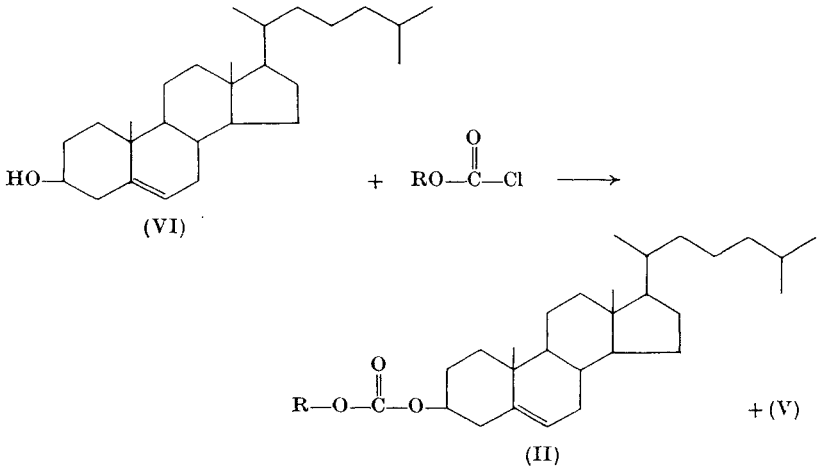
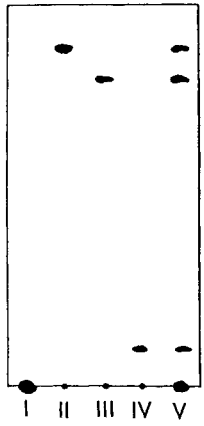


Figure 1 shows the thin-layer chromatographic separation of the reaction products on Silica Gel H with cyclohexane as developing solvent.



I cholesteryl ethyl carbonate
II cholesta-3,5-diene
III 3β-chloro-cholest-5-ene
IV di-cholesteryl carbonate
V mixture I–IV

Figure 1.

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TABLE 1 Cholesteryl Alkyl Carbonates

R(alkyl)	Yield (%)	m.p. (°C)	c.p. (°C)	Formula	Mol. wt.	Analytical values (%) Calculated C	Calculated H	Found C	Found H
Amyl	73	98	102	$C_{33}H_{56}O_3$	500.9	79.14	11.27	79.26	11.11
Hexyl	79.7	106	108	$C_{34}H_{58}O_3$	514.8	79.32	11.35	79.16	11.10
Heptyl	75.7	79	85	$C_{35}H_{60}O_3$	528.8	79.49	11.43	79.30	11.41
Octyl	70.3	53	83	$C_{36}H_{62}O_3$	542.9	79.64	11.51	79.91	11.62
Nonyl	75.5	78	81	$C_{37}H_{64}O_3$	556.9	79.79	11.58	79.61	11.79
Decyl	77	76	79.5	$C_{38}H_{66}O_3$	570.9	79.94	11.65	80.11	11.86
Undecyl	76	53	78	$C_{39}H_{68}O_3$	584.9	80.07	11.72	80.19	11.55
Dodecyl	78.5	62.5	76	$C_{40}H_{70}O_3$	599.0	80.21	11.78	79.91	11.54
Tetradecyl	80	70	75	$C_{42}H_{74}O_3$	627.0	80.45	11.90	80.20	11.83
Hexadecyl	78	69	75	$C_{44}H_{78}O_3$	655.1	80.67	12.00	80.45	12.08
Octadecyl	79	79.5	81	$C_{46}H_{82}O_3$	683.1	80.87	12.10	80.66	12.18
Eicosyl	79	69	71	$C_{48}H_{86}O_3$	711.2	81.06	12.19	80.97	12.09
Docosyl	75.6	70	81	$C_{50}H_{90}O_3$	739.2	81.23	12.27	81.35	12.26

For purification the crude material was chromatographed on Silica Gel and eluted with a 30/70 mixture of benzene/ligroine, where cholesta-3,5-diene and 3β-chloro-cholest-5-ene are eluted first, followed by di-cholesteryl carbonate and the corresponding cholesteryl alkyl carbonate, while unreacted cholesterol is held back on the column. The fractions were monitored by thin-layer chromatography for the presence of impurities, and then the material was recrystallized from acetone or butanone for the higher members. The yield of chromatographically pure material was above 70%. The melting (m.p.) and clearing (c.p.) points were obtained in an open capillary and are not corrected. The melting points are transitions from the solid to the mesophase. The physical properties and yields, with supporting analytical data are found in Table 1.

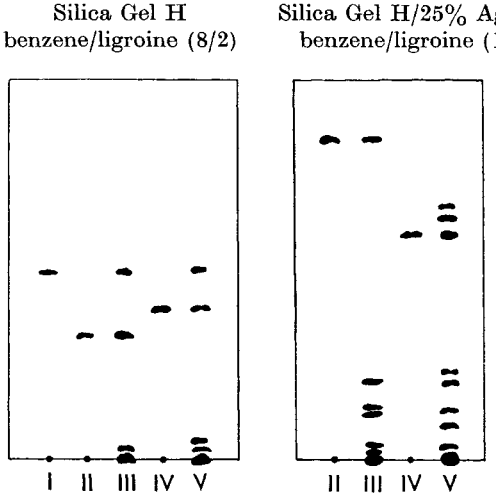

Figure 2.

I di-cholesteryl carbonate
II cholesteryl octyl carbonate
III cholesteryl octyl carbonate, oxidized
IV cholesteryl erucyl carbonate
V cholesteryl erucyl carbonate, oxidized

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II. Stability

Compared with cholesteryl esters, the cholesteryl alkyl carbonates are less stable. At higher temperatures they undergo Tschugaev rearrangement to cholesta-3,5-diene, carbon dioxide and the corresponding alkanol,[7, 8] similar to the thermal decomposition of the even less stable cholesteryl alkyl xanthates.[9, 10, 11, 7, 8] At room temperature, over a period of several months, various products are formed, two of which could be identified as cholesterol and di-cholesteryl carbonate. Using silver nitrate-impregnated Silica Gel,[12, 13] a much better separation of the oxidation and rearrangement products is achieved, as shown in the case of cholesteryl octyl and cholesteryl erucyl carbonate (Fig. 2).

III. Infrared Spectra

The reported ester carbonyl vibration of carbonates[14, 15, 16] at 1740–1750 cm^{-1} is found in the cholesteryl alkyl carbonates at

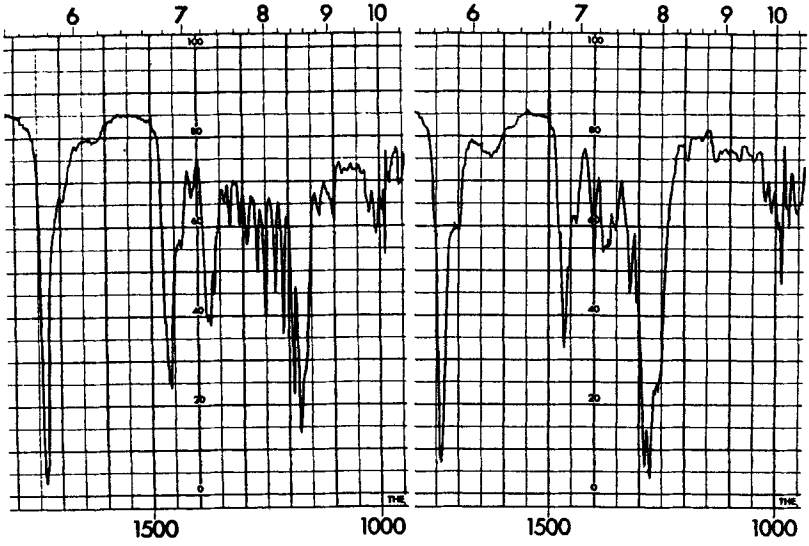

Figure 3. Infrared spectra, between 1000 and 1700 cm^{-1}, of cholesteryl octadecanoate and cholesteryl octadecyl carbonate.

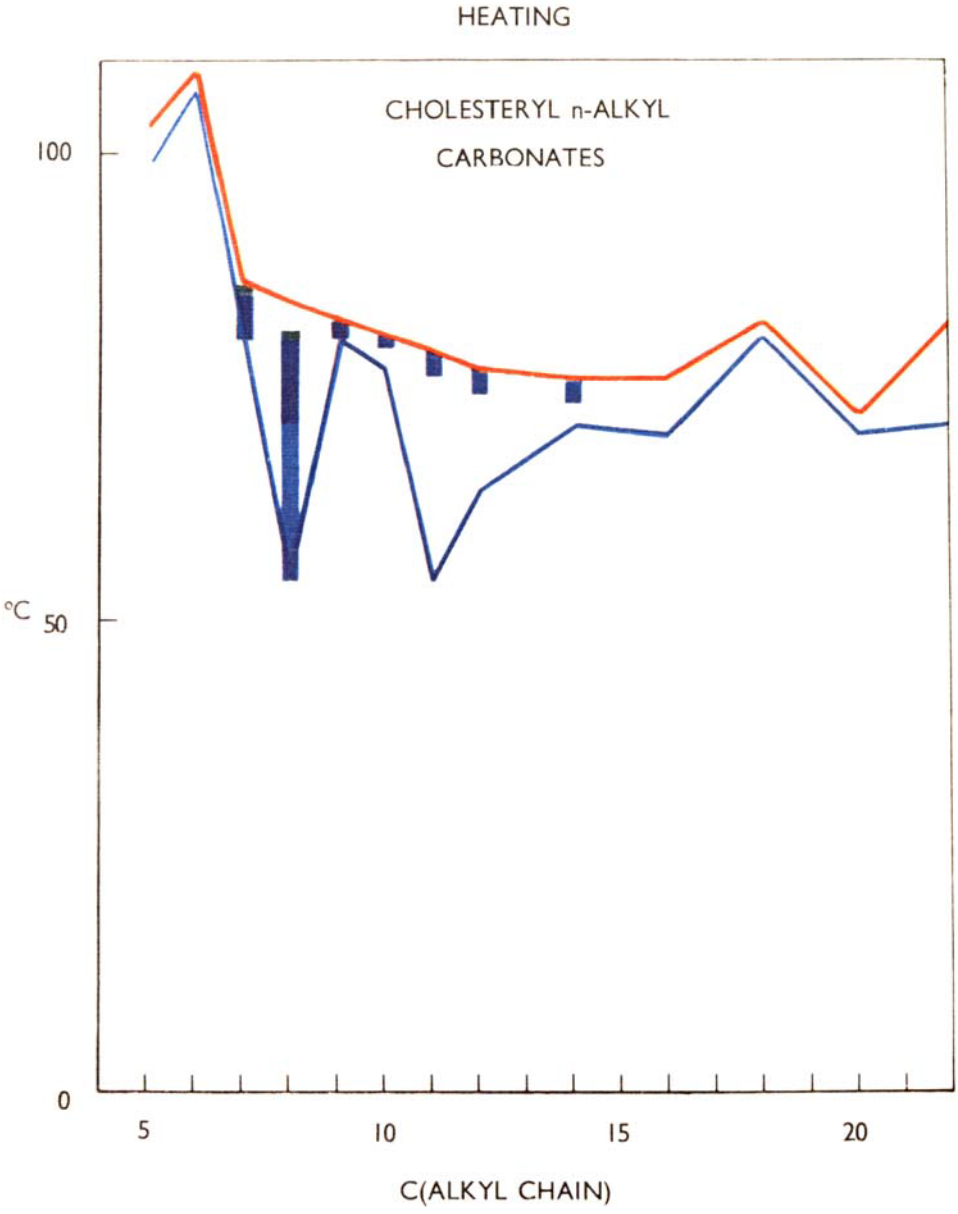

Figure 1.

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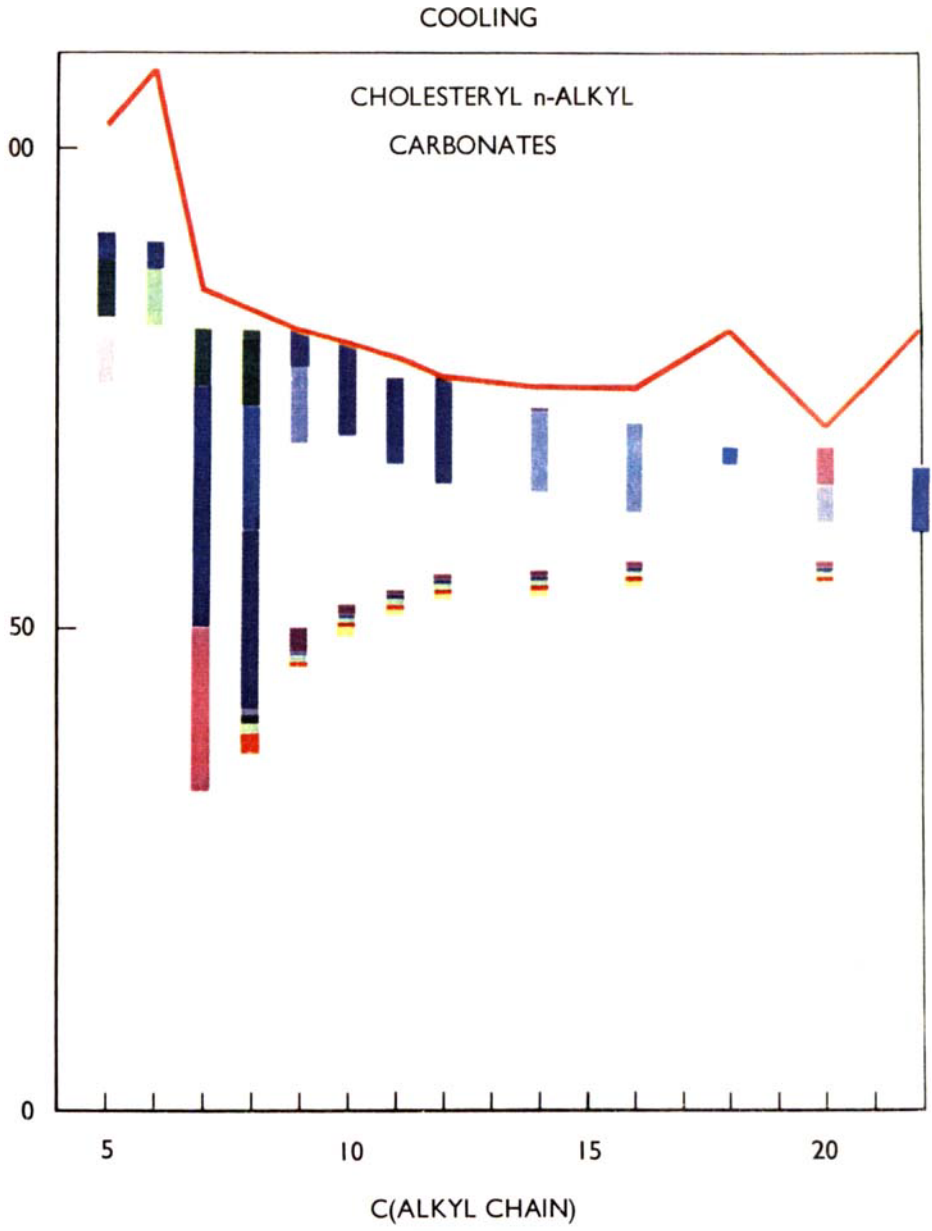

Figure 2.

1735–1741 cm^{-1}, and the C—O vibration (1260–1280 cm^{-1}) at 1265–1275 cm^{-1}. Cholesteryl esters have the strongest carbonyl band near 1170 cm^{-1}. Due to this shift to shorter wavelengths, the observed band progression in cholesteryl esters[17,18] cannot be observed in the carbonates, as shown in Fig. 3.

IV. Properties

Cholesteryl amyl carbonate melts at 98° and clears at 102°. Cooling gives a blue color at 91°, which changes to green-blue at 88° and disappears at 82°. A light violet color starts at 80° and disappears at 75°, the solidification point.

Cholesteryl hexyl carbonate melts at 106° and clears at 108°. Cooling gives a blue color at 90°, which turns green at 87° and disappears at the solidification point of 81°.

Cholesteryl heptyl carbonate gives a dark blue melt at 79°, turns at 84° to a very brilliant green-blue, which disappears at the clearing point of 85°. On cooling, green-blue starts at 81° and changes to dark blue at 75°. On further cooling, the color slowly turns to blue violet until the melt solidifies at 33°.

Cholesteryl octyl carbonate gives a light blue melt at 53°, which darkens near 70°, changes to a brilliant green-blue at 79°, which disappears near 80° and clears at 83°. Cooling gives a green-blue color near 81°, becoming very intense at 80°, changes slowly to blue (73°), which gets more intense near 60° and very intense near 50°, turning to a brilliant light blue at 41.5°, to green-blue at 41°, to green at 40°, to red at 39°, to a yellowish red at 38°, and finally solidifies at 37°.

Cholesteryl nonyl carbonate melts at 78° and turns to a deep blue at 79°, which disappears at 81°, the clearing point. On cooling, the blue color starts at 81°, changes to light blue near 77°, and is colorless at 69°. Further cooling gives violet at 50°, an intense violet at 49°, light blue at 47.5°, green at 47°, a brilliant red at 46.5°, and solidification at 46°.

Cholesteryl decyl carbonate melts at 76°, turns blue at 78°, and clears at 79.5°. On cooling, blue starts at 79° and disappears at 70°.

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Violet starts at 52.5°, turns to a brilliant light blue at 51.5°, to green at 51°, to red at 50.5°, to yellow at 50°. The solidification point is 49.5°.

Cholesteryl undecyl carbonate melts at 53°, turns blue at 75°, and clears at 78°. Cooling gives a blue color at 76°, which disappears at 67°. Violet begins at 54°, changes to blue at 53.5° to green at 53.3°, to red at 53°, to yellow at 52.5°. It solidifies at 52°.

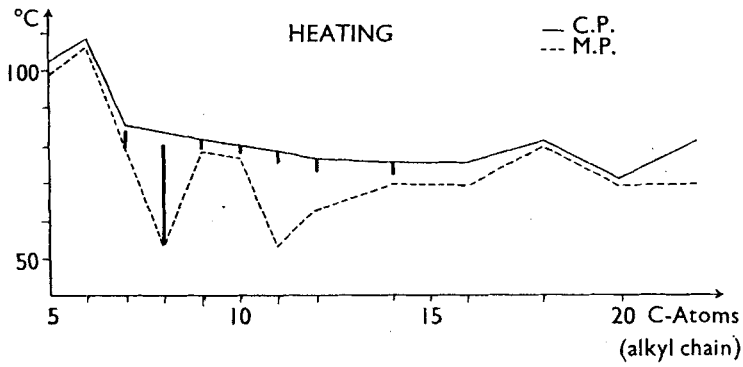

Fig 4

Cholesteryl dodecyl carbonate melts at 62.5°, turns blue at 73°, and clears at 76°. A deep blue color begins at 76° when cooling and disappears at 65°. Further cooling gives violet at 55.5°, blue at 55°, green at 54.5°, red at 54°, yellow-red at 53.5°, and solidification at 53°.

Cholesteryl tetradecyl carbonate melts at 70°, turns dark blue at 72°, and clears at 75°. On cooling, dark blue begins at 73°, changes to light blue at 72.5°, which disappears at 64°. Violet starts at 56°, turns blue at 55.5°, green at 55.3°, red at 55°, yellow at 54.5°, and solidifies at 54°.

Cholesteryl hexadecyl carbonate melts at 69°, clears at 75°, and on cooling turns light blue at 71.5°, which disappears at 62°. Violet starts at 57°, changes to green at 56.5°, red and yellow near 55.5°, and solidifies at 55°.

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Cholesteryl octadecyl carbonate which melts at 79.5° and clears at 81°, gives a blue color at 69° on cooling which disappears at 67°, the solidification point.

Cholesteryl eicosyl carbonate melts at 69° and clears at 71°. Cooling gives a blue violet color at 69°, which slowly fades and disappears at 61°. At 57° violet starts, turning blue at 56.8°, green at 56.5°, red at 56.3°, and colorless at 56°, the solidification point.

Cholesteryl docosyl carbonate melts at 70° and clears at 81° and on cooling turns blue at 67° and colorless at the solidification point (60°).

Figures 4 and 5 graphically illustrate the transition points of the prepared cholesteryl alkyl carbonates with increasing chain length and the color zones on heating (Fig. 4) and cooling (Fig. 5).

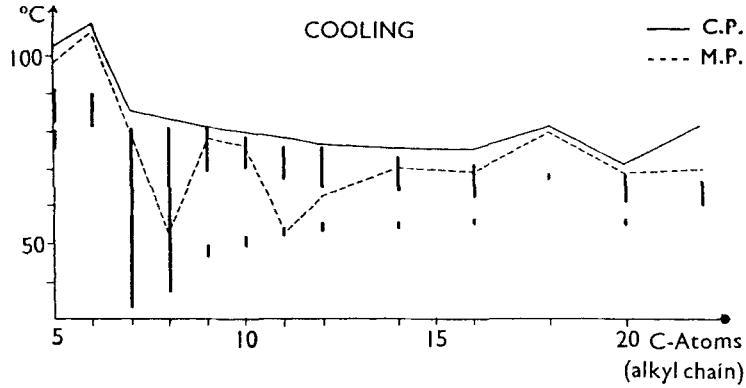

Fig 5

V. Investigation in the Capillary

With the physical properties, obtained in a capillary, summarized in Figs. 4 and 5, four different groups can be distinguished:

(1) The first two members, cholesteryl amyl and hexyl carbonate, show the high-temperature color band only on cooling.

(2) The next two members, cholesteryl heptyl and octyl carbonate, give the high-temperature color band both on heating and cooling, followed by the low-temperature color band on further cooling without an interruption of the color sequence.

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(3) The next five members, cholesteryl nonyl through tetradecyl carbonate, give the high-temperature color band on heating and on cooling, which disappears on further cooling and then is followed by the low-temperature color band.

(4) The last four members, cholesteryl hexadecyl through docosyl carbonate, give the high-temperature color band only on cooling, followed by the low-temperature color band, with the exception of the solidifying cholesteryl octadecyl and docosyl carbonate.

These findings indicate that with an alkyl chain longer than six C-atoms two cholesteric mesophases are present, because both change colors with a change in temperature. The low-temperature color band, consisting of the solar spectrum, is always monotropic. The high-temperature color band exhibiting only parts of the solar spectrum (mostly from blue to green) is enantiotropic with an alkyl chain consisting of six to fourteen C-atoms, and monotropic for the lower and higher members.

VI. Investigation with the Polarizing Microscope

The observations, made with crossed polarizers and white light in both transmission and reflection essentially supported the observations made in the capillary. One representative of this series, cholesteryl tetradecyl carbonate, was selected and the results shall be explained in detail.

(a) *Reflection*

(1) Careful heating of the solid to the enantiotropic range of the high-temperature color band produces a blotchy structure of blue or green colors, depending on the temperature.

(2) On cooling the color disappears with a birefringent pattern growing into the plane texture. It looks like a spherulite with a Maltese cross, but consists of more or less radially aligned ellipses and hyperbola. It can therefore be concluded that this is a particular arrangement of the focal-conic cholesteric texture, since it can coexist with the plane texture.

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(3) A significant feature of this high-temperature color band is its sensitivity to slight mechanical disturbance, because it disappears immediately on touching the cover slide. Further cooling and touching then again produces the low-temperature color band.

(b) *Transmission*

(1) On heating the solid above the melting point, a cholesteric mesophase with a negative optical sign can be observed before the transition to the isotropic liquid, but no colors are visible.

(2) On cooling of the isotropic liquid the high-temperature color band cannot be observed. Below the melting point temperature a cholesteric texture with crosses of optical negative sign appears. On further cooling this changes to a smectic mesophase below the temperature range in which the low-temperature color band can be observed.

(3) If the foregoing cholesteric mesophase is mechanically disturbed in the range of this color band, selectively reflected light is exhibited, covering the range of the solar spectrum.

The enantiotropic high-temperature color band was discovered in the capillary. Due to its sensitivity to mechanical disturbance, it took quite some effort to realize these observations between cover slides under the microscope. This is in contrast to the monotropic low-temperature color band, which is easily produced by disturbing the cholesteric mesophase in its temperature range.

VII. Summary

(1) Two different color bands were observed, which is very unusual. Obviously they belong to the same cholesteric phase, as it was determined by very sensitive calorimetric measurements.

(2) The enantiotropic high-temperature color band is actually destroyed by the slightest mechanical disturbance. This is in contrast to the ordinary experience, where the plane texture occurs either spontaneously or by mechanical disturbance.

(3) The observed selectively scattered light of approximately the same intensity in both transmission and reflection is also very unusual for a cholesteric phase.

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An interpretation of these unusual observations is not possible at present, since one even does not exactly understand the structure or mechanism within the cholesteric mesophase.

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VIII. Acknowledgments

It is a pleasure to thank Mr. R. Sherman for many measurements and Mr. A. Brown for experimental help. Thanks are also due to Drs. R. Ennulat and J. Muller for many stimulating discussions.

IX. Experimental Section

Thin-layer chromatography: Ascending thin-layer chromatography was performed on 0.25 mm layers of Silica Gel H. The compounds were visualized by charring with sulfuric acid.

Column chromatography: Silica Gel for Chromatography, 80–200 mesh, was used without pretreatment. The columns were prepared in benzene/ligroine (15/85) and the same solvent mixture used for elution. The ligroine used had b.p. 65–75°. The fractions were monitored for the presence of impurities by thin-layer chromatography.

Infrared spectra were recorded on a Perkin-Elmer Model 421 double-beam grating spectrometer. The compounds were examined in potassium bromide discs.

Preparation of compounds: The general synthesis procedure is exemplified by one experiment. The proportion of reactants and solvents were the same in all procedures. The reactions were run in an oxygen-free atmosphere of nitrogen.

Cholesteryl alkyl carbonates

(1) To a stirred solution of 0.01 mole of cholesteryl chloroformate† [6] and 0.01 mole of n-alkanol in 50 ml of absolute benzene a solution of 0.01 mole of pyridine in 10 ml. of absolute benzene is added in the course of 40 min. Stirring is continued for 2 hr at

† Commercially available from Aldrich Chemicals, Milwaukee, Wisc. and Distillation Products, Rochester, New York.

room temperature and another 2 hr under reflux. After removal of the precipitated pyridine hydrochloride, the solution is taken to dryness, and the residue chromatographed on a Silica Gel column. The fractions containing the alkyl carbonate are combined, the solvent is removed, and the residue recrystallized from acetone or from butanone for the higher members. Preparative and analytical data appear in Table 1.

(2) Under exactly the same conditions from 0.01 mole of purified cholesterol[19] and 0.01 mole of the corresponding alkyl chloroformate in the presence of 0.01 mole of pyridine in essentially the same yield after chromatographic purification.

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REFERENCES

1. Gray, G. W., *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, Inc., New York, New York (1962).
2. Gray, G. W., *J. Chem. Soc.* 3733 (1956), and references cited therein.
3. Däumer, E., Dissertation, Halle-Wittenberg (1912).
4. Lenk, B., Dissertation, Halle-Wittenberg (1913).
5. Dorn, E., *Phys. Z.* **11**, 777 (1910).
6. McKay, A. F. and Vavasour, G. R., *Canad. J. Chem.* **31**, 688 (1953).
7. O'Connor, G. L. and Nace, H. R., *J. Am. Chem. Soc.* **74**, 5454 (1952).
8. O'Connor, G. L. and Nace, H. R., ibid. **75**, 2118 (1953).
9. Tschugaeff, L. and Gasteff, A., *Chem. Ber.* **42**, 4631 (1909).
10. Tschugaeff, L. and Fomin, W., *Ann.* **375**, 288, 293 (1910).
11. Eck, J. C., v. Peursem, L., and Hollingsworth, E. W., *J. Am. Chem. Soc.* **61**, 171 (1939).
12. Barrett, C. B., Dallas, M. S. J. and Padley, F. B., *Chem. Ind.* (*Lond.*) 1050 (1962).
13. Morris, L. J., ibid 1238 (1962).
14. Hales, J. L., Jones, J. I., and Kynaston, W., *J. Chem. Soc.* 618 (1957).
15. Mecke, R., Mecke, R., and Lüttringhaus, A., *Z. Naturf.* **10b**, 365 (1955).
16. Thompson, H. W. and Jameson, D. A., *Spectrochim. Acta* **13**, 236 (1958).
17. Labarrère, J. A., Chipault, J. R., and Lundberg, W. O., *Anal. Chem.* **30**, 1466 (1958).
18. Carruthers, W. and Plimmer, J. R., *J. Chem. Soc.* 3257 (1962).
19. Fieser, L. F., *J. Am. Chem. Soc.* **75**, 5421 (1953).