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Structure and Mesomorphism of Cholesteric Liquid Crystals

Odessa, 1985

A. I. Galatina, N. S. Novikova, L. G. Derkach, N. L. Kramarenko,
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INTRODUCTION

Liquid crystals have become an object for the attention of investigators from many countries for about twenty years. This is due, first of all, to their practical applications. These are really numerous: indicators for electronics, thermoindicators, analyzers for the pollution of the environment, means for the visualization of pictures, designs of optical treatment of information, etc. Besides, liquid crystals are unique compounds of great interest from the viewpoint of the molecular physics of the condensed state.

Interaction of molecules, mainly of organic compounds of definite structure forming complex ordered "ensembles," the so-called supramolecular structures, results in the formation of the liquid crystalline state—a liquid crystal.

In 1978 J.-M. Lehn[1] introduced the notion of supramolecular chemistry—a branch of science dealing with such supramolecular structures.

Supramolecular structure of cholesteric liquid crystals (CLC) seems to be of special interest. However, since this structure is the most complex one as compared with the other mesophase types CLC are still the least studied. It is known that parameters of the supramolecular structure of CLC, such as helical pitch, order parameter depending on a number of factors—temperature, pressure and, to a less degree, on the electrical and magnetic fields, etc.—determine their optical characteristics and, hence, their application.

It is also known that the possibility of the formation of the liquid crystalline state depends on the ability of the initial molecules—mesomorphogens to give ordered systems resulting from intermolecular interaction which, in turn, depends on the molecular structure of the compounds.

Thus, the establishment of the correlation between the chemical structure of molecules—mesomorphogens, parameters of their supramolecular structure and mesomorphic properties, is the foundation for investigations in the liquid crystals branch of chemistry. Establishment of this dependence will allow, on the one hand to elaborate the requirements of the structure of the molecules capable to form the liquid crystalline state, and on the other hand to accomplish the directed synthesis of liquid crystals with the given properties.

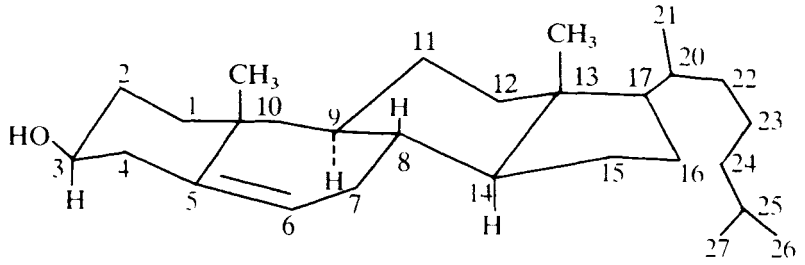
This question has been studied for a rather long time. Already in '40 Wiegand[2,3] studied the mesomorphic properties of different steroids. He investigated the effect of the steric configuration of the steroid ring system, conformation of substituents and the position of

the double bond in cyclopentanperhydrophenanthrene fragment on the ability of different steroid derivatives for mesomorphism. The monograph by Gray[4] contains the most detailed and comprehensive data on the interdependence of chemical structure and mesogenic properties of organic compounds. At present, some empirical connections are found between the structure and mesomorphic properties of a number of cholesteric liquid crystals reported earlier in Ref. 5.

The present work is aimed at summarizing some literature data and some results obtained by the authors on the study of the interconnection of molecular structure of a number of cholesteric liquid crystals synthesized based on cholesterine and thiocholesterine with the parameters of the supramolecular structure as well as with their mesomorphic properties.

1. MOLECULAR STRUCTURE AND MESOMORPHISM OF STEROID DERIVATIVES

The appearance of the cholesteric mesophase (CMP) of steroid derivatives is due to their chirality.[4,6–8] The stereochemical configuration of cholesterine looks as follows:



Since in the formation of CMP the terminal interactions of the molecules[9,10] are of special importance, results given in Refs. 11 and 12 indicate the necessity of taking into account different effects of different parts of a molecule on the mesophase properties. In case of cholesterine and its derivatives it is possible to note following structural elements:

1. Cyclopentanperhydrophenanthrene fragment;
2. alkyl chain in 17th position of the steroid fragment;
3. substituent in 3rd position of the system of steroid rings.

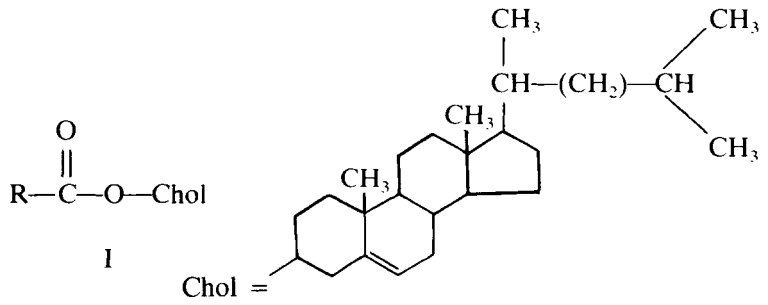
Systematic study of the effect of these elements on mesomorphic properties of the steroids was not carried out, however, there are

literature data[5,10,13,14] on some changes of their structure determining the possibility of mesophase existence.

1.1. Cholesterine derivatives

1.1.1. Esters of cholesterine and saturated carboxylic acids

Cholesterylalkanoates are described and studied in the literature more than any other cholesterine alkanoate (I).



I

R = H, C_nH_{2n+1}; n = 1–19

Methods of synthesis of cholesterylalkanoates are described in Refs. 4, 7, and 15–19. Their mesomorphic properties are investigated in Ref. 15.

It is seen from the data of Table 1 that the first members of this homologous series (R = H, CH_3) are characterized by monotropic cholesteric mesophase, while for the next homologues the mesophase becomes enantiotropic. From the 7th homologue smectic mesophase is observed. This change of mesomorphic characteristics of cholesterylalkanoates is due to the specific effect of *n*-alkyl radicals which is also indicated by the similar character of the change of mesomorphic properties within the homologous series of thiocholesterine.[20]

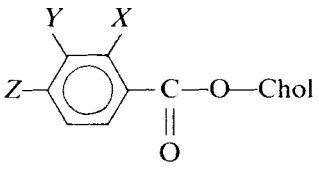
Substitution of the aliphatic radical in the ester moiety for the aromatic one results, as a rule, in the broadening of the range of mesophase existence and in the increase of the temperatures of the phase transitions. Here high temperature (100–250°C) and thermally stable (existence interval 50–100°C) cholesteric mesophase is formed. This can be explained by the effect of conjugation of the aromatic radical (phenyl, naphthyl) with the carbonyl group of the ester moiety. In fact, the removal of the phenyl radical from the C=O group results in the decrease of the temperature of the phase transitions.

TABLE 1

Mesomorphic characteristics of cholesterylalkanoates (I)

No	*R*	Temperature of phase transition, °C		
		T_{sm}	T_{ch}	T_{is}
1	H	—	(60.5)	97.5
2	CH_3	—	(94.5)	116.5
3	C_2H_5	—	95.2	111.8
4	C_3H_7	—	102.0	113.0
5	C_4H_9	—	93.0	101.5
6	C_5H_{11}	—	99.5	101.5
7	C_6H_{13}	(92.5)	(95.5)	114.0
8	C_7H_{15}	(69.5)	(96.5)	110.0
9	C_8H_{17}	(77.5)	80.5	92.0
10	C_9H_{19}	(81.5)	85.5	92.5
11	$C_{10}H_{21}$	(81.9)	(90.0)	92.5
12	$C_{11}H_{23}$	(81.5)	(87.8)	92.0
13	$C_{12}H_{25}$	63.5	78.8	84.8
14	$C_{13}H_{27}$	71.4	79.3	84.1
15	$C_{14}H_{29}$	70.0	78.3	82.9
16	$C_{15}H_{31}$	(72.0)	76.3	79.8
17	$C_{16}H_{33}$	(76.5)	78.0	80.6
18	$C_{17}H_{35}$	75.5	79.5	83.0
19	$C_{18}H_{37}$	(74.2)	(77.8)	82.0
20	$C_{19}H_{39}$	(74.3)	(78.1)	85.0

Study of the effect of the molecular structure of esters of cholesterine and aromatic acids on their mesomorphic properties is being given consideration. These data are summarized in the works of Indian chemists. In Ref. 21 cholesterine benzoates are described containing stereoregular substituents in different positions of the phenyl radical (II).



II

a) X = Cl, Br, I, CH_3, NO_2; Y,Z = H
b) Y = Cl, Br, I, CH_3, NO_2; X,Z = H
c) Z = Cl, Br, I, CH_3, NO_2, C_6H_5; Y,X = H

The temperatures of the phase transitions of a number of monosubstituted benzoates are given in Table 2. It was found that *o*- and *p*-derivatives show enantiotropic cholesteric mesophase, while *m*-derivatives—monotropic one. *n*-Substitution results in the increase of the temperature of isotropic transition as compared with unsub-

TABLE 2

Mesomorphic characteristics of cholesterylbenzoates (II)

No	X	Y	Z	Temperature of phase transition, °C	
				T_{ch}	T_{is}
1	H	H	H	150.0	178.0
2	Cl	—	—	106.0	146.0
3	Br	—	—	105.0	134.0
4	I	—	—	108.0	112.0
5	CH_3	—	—	110.0	134.0
6	NO_2	—	—	150.0	156.9
7	—	Cl	—	(146.5)	147.0
8	—	Br	—	(135.0)	142.0
9	—	I	—	(113.0)	130.0
10	—	CH_3	—	(130.0)	143.5
11	—	NO_2	—	140.0	174.0
12	—	—	Cl	170.0	257.0
13	—	—	Br	170.0	257.5
14	—	—	I	178.0	252.0
15	—	—	CH_3	179.0	246.0
16	—	—	NO_2	191.5	260.0
17	—	—	C_6H_5	179.0	290.0

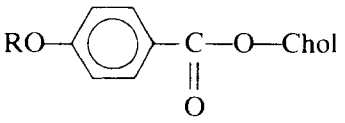
stituted cholesterine benzoate, whereas the substitution in *o*- and *m*-position results in its decrease.

Higher temperatures of transitions into isotropic liquid (IL) and enantiotropic mesomorphism of *p*-substituted cholesterine alkanoates are explained by the linearity of the molecules and by the presence of a polar substituent at their terminal. According to their effect on the mesomorphic characteristics the substituents form the following series:

$$C_6H_5 > CH_3O > NO_2 > Br > Cl > I > CH_3 > H$$

In the case of *m*-substituted derivatives the substituent reduces the anisotropy of the molecules which impedes, as the authors suggest, their layer packing within the crystalline lattice and the compound melts directly into the isotropic liquid. Upon cooling the possibility appears of the mutual orientation of the molecules to give the monotropic phase. Cholesteryl-*m*-nitrobenzoate forming enantiotropic cholesteric mesophase is the exception. The increase of thermal stability and the appearance of the enantiotropic mesophase in this case are due to the high polarity of the nitro-group. The decrease of the temperatures of the phase transitions for *o*-substituted cholesterine benzoates is connected, as in the case of *m*-substituted ones, with the increase of the molecular width.

The same authors have described the homologous series of cholesterine *p*-*n*-alkoxybenzoates.[22] In this work synthesis is described, as well as the methods for the compound purification, determination of the phase transition temperatures by polarizing microscopy. The dependences of the phase transition temperatures on the length of the *n*-alkyl radical are summarized in Table 3.



$R = C_nH_{2n+1}$
$n = 1-10, 12, 16, 18$

III

It was noted that for all the compounds described enantiotropic mesophase is characteristic and beginning from the 7th member of the homologous series, in addition to the cholesteric mesophase, the smectic one is also observed.

The authors draw an analogy of the studied series with the cholesterylalkanoates. The appearance of the smectic mesophase of cholesterylbenzoates with the long hydrocarbon chain in the 3β-position of cholesterine is due to the increase of the side and the weakening of the terminal intermolecular interactions.

In Refs. 23 and 24 data are given on the diagrams of state and

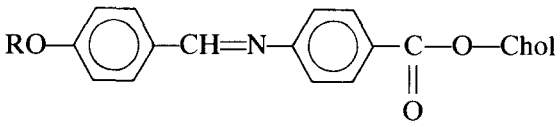
TABLE 3

Mesomorphic characteristics of cholesterine *p*-*n*-alkoxybenzoates (III)

No	*R*	Temperature of phase transitions, °C		
		T_{sm}	T_{ch}	T_{is}
1	CH_3	—	180.0	268.0
2	C_2H_5	—	149.5	265.0
3	C_3H_7	—	141.0	253.0
4	C_4H_9	—	134.0	248.0
5	C_5H_{11}	—	148.5	236.5
6	C_6H_{13}	—	150.0	234.5
7	C_7H_{15}	138.5	160.5	222.0
8	C_8H_{17}	138.0	171.5	220.5
9	C_9H_{19}	128.0	176.0	213.0
10	$C_{10}H_{21}$	110.0	177.5	209.0
11	$C_{12}H_{25}$	128.0	179.5	200.5
12	$C_{16}H_{33}$	92.0	170.5	179.5
13	$C_{18}H_{37}$	47.0	161.0	163.0

electrooptic properties of 2,4-, and 3,4-dichloro and 3,5-dinitrobenzoates.

Mesogeneity of *p*-*n*-alkoxybenzylidene-*p*-benzoates of cholesterine was also studied, their synthesis given in Ref. 25.

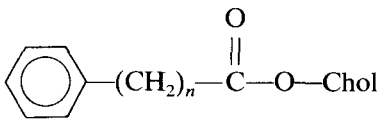


IV

$R = C_nH_{2n+1}$
$n = 1-10, 12, 16, 18$

Synthesized cholesterine derivatives possess high temperature cholesteric mesophase; at the transition to the isotropic liquid the above compounds decompose. Homologues with $n = 1-6$ are characterized by enantiotropic cholesteric mesophase. Beginning from the seventh homologue smectics are observed.

Elser and Pohlmann[26] worked out a procedure for the preparation of cholesterine ω-phenylalkanoates (V):



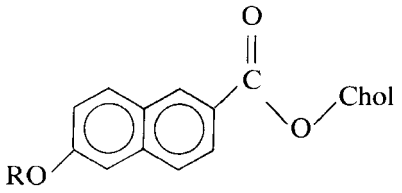
V $n = 1-15$

Initial ω-phenylsubstituted saturated monocarboxylic acids were prepared from the ester chlorides of α, ω-dicarboxylic acids.

Cholesterine ω-phenylalkanoates were obtained in the presence of 1,1-carbonyldiimidazole as a catalyst. Phase transitions of the synthesized compounds were studied in Ref. 27.

The first homologue shows no mesomorphism which is perhaps due to the disorder of the geometric anisotropy of the molecule, the next five homologues possess cholesteric mesophase and beginning from cholesterine ω-phenylcaprylate the smectic mesophase appears. It should be noted that some compounds of this series possess high thermal sensitivity (mesophase interval 0.6°C), which is valuable for their practical application.

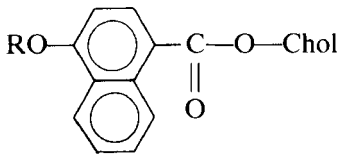
In Ref. 28 synthesis and properties of cholesterine 6-*n*-alkoxy-2-naphthanoates are described (VI).



$R = C_nH_{2n+1}$
$n = 1-10, 12, 16, 18$

VI

Compounds of this homologous series are obtained by means of condensation of 6-*n*-alkoxy-2-naphthoic acids chlorides with cholesterine in the presence of dimethylaniline at $T = 150°C$. All the mentioned esters possess enantiotropic cholesteric mesomorphism; beginning from the 5th homologue the smectic mesophase appears. In the work cited[29] the synthesis of cholesterine 4-*n*-alkoxy-1-naphthanoate was also carried out (VII).

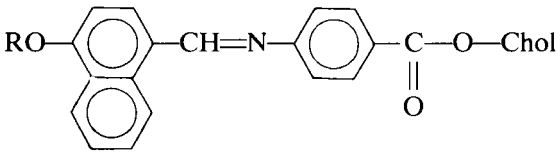


R = alkyl

VII

Within this series mesophase is less thermostable. It should be noted that, although the presence of condensed benzene rings in the acyl radical increases molecular polarizability, the degradation of the mesomorphic characteristics of these compounds is due to the decrease of their geometric anisotropy owing to 1,4-substitution in the naphthalene fragment.

In continuation of this work the synthesis of cholesterine 4-*n*-alkoxy-1-naphthylidene-*n*-aminobenzoates was carried out:[29]



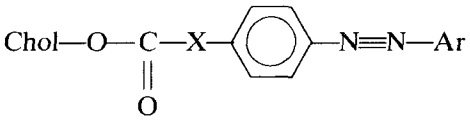
$R = C_nH_{2n+1}$
$n = 1-10, 12, 14, 16, 18$

VIII

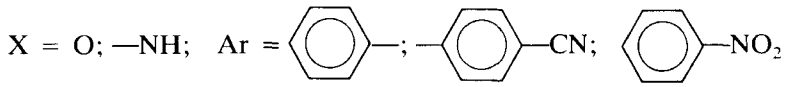
All the members of this homologous series possess enantiotropic cholesteric mesophase with a wide temperature range of existence

(50–100°C). The 12th homologue forms monotropic smectic mesophase which is transformed into enantiotropic one for the subsequent homologues.

Synthesis of liquid crystalline dyes of the common formula (IX) has been reported[31]



IX

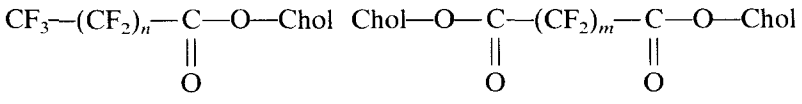


which are promising for technology. These compounds possess high temperature enantiotropic cholesteric mesomorphism over a wide temperature range. In the work cited it is concluded that the introduction of substituents decreasing the electron density of the azobenzene fragment results in the increase of the phase transition temperatures.

1.1.2. Esters of cholesterine and halogensubstituted saturated carboxylic acids

Literature data on the esters of cholesterine and halogensubstituted carboxylic acids are rather limited. In Ref. 32 cholesterine β-chloropropionate is referred to as an effective stabilizing agent of liquid crystalline compositions. Synthesis of cholesteryl esters of perfluoroalkancarboxylic acids is also reported.[33] It was shown that substitution of hydrogen atoms of acyl fragment of the ester for fluorine results in the decrease of the transition temperatures to isotropic liquid and cholesteric mesophase.

These compounds possess monotropic cholesteric mesophase with the range of existence from 3 to 10°C. Esters of perfluorodicarboxylic acids and cholesterine show enantiotropic cholesteric mesophase (X, XI).



X

$n = 1–6$

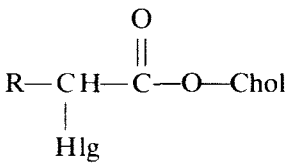
XI

$m = 2–5$

In the present paper data are summarized on the systematic synthesis of cholesterine esters of α, β and γ-halogensubstituted saturated carboxylic acids, their mesomorphic properties are described, and the connection of their properties with the molecular structure of the compounds is revealed.[34]

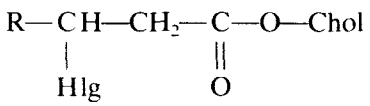
Esters of cholesterine and halogensubstituted carboxylic acids were prepared by condensation of the corresponding acid chlorides with cholesterine in a non-polar solvent in the presence of pyridine.[34–37]

The following compounds were prepared:



R = H, C_nH_{2n+1}
Hlg = Cl, Br
n = 1–5, 7, 16

XII



R = H, CH_3, CH_2Cl
Hlg = Cl, Br

XIII

Mesomorphic properties of the synthesized compounds were studied by polarizing microscopy and are summarized in Table 4.

Identity of the compounds obtained was proved by thin layer chromatography and their composition and structure were determined based on microanalysis, IR and PMR spectroscopy (Table 5).

In the IR spectra of all the compounds synthesized a band is present in the region 1745–1730 cm^{-1} characteristic of the stretching vibrations of the C=O group in esters and there are two bands of average intensity within the range 1250–1170 cm^{-1} corresponding to the stretching vibrations of the C—O—C bond. The presence of halogen is proved by absorption bands at 840–800 cm^{-1} (C—Cl bond) and 630–590 cm^{-1} (C—Br bond). The absorption band of the carbonyl bond in unsubstituted analogues—cholesterylalkanoates is located at 1730 cm^{-1}. Substitution of hydrogen for halogen at the neighbouring carbon atom of the carbonyl group results in the shift of its absorption band by 10–15 cm^{-1} due to the inductive effect of the halogen. According to the data of Table 5 the inductive effect of halogen in

TABLE 4

Mesomorphic characteristics of halogensubstituted cholesterylalkanoates (XII and XIII)

No	R	Halogen		Temperature of phase transition °C		
		XII	XIII	T_{cryst}	T_{chol}	T_{is}
1	H	Cl	—	—	—	164.0
2	CH_3—	Cl	—	—	—	122.0
3	CH_3—	Br	—	—	—	127.0
4	$(CH_3)_2$—	Br	—	—	—	176.0
5	CH_3CH_2—	Cl	—	—	—	114.0
6	CH_3CH_2—	Br	—	—	—	106.0
7	$(CH_3)_2C$—	Cl	—	—	—	138.0
8	$(CH_3)_2CH$—	Br	—	—	—	142.0
9	$CH_3(CH_2)_2$—	Cl	—	(67.0)	69.0	72.0
10	$CH_3(CH_2)_2$—	Br	—	(62.0)	73.0	74.0
11	$CH_3(CH_2)_3$—	Br	—	(46.0)	49.0	55.0
12	$CH_3(CH_2)_4$—	Cl	—	(50.0)	(55.0)	78.0
13	$CH_3(CH_2)_6$—	Cl	—	(46.5; 50.0*)	60.0 (56)	64.4
14	$CH_3(CH_2)_{15}$—	Br	—	room*	47.3	50.5
15	H	—	Cl	(50.6)	85.8	129.0
16	H	—	Br	(62.0)	92.0	120.0
17	CH_3—	—	Cl	(112.0)	121.0	123.0
18**	CH_2Cl	—	—	(73.0)	82.0	89.0
19	CH_3—	—	Br	(95.0)	105.0	110.0

* Temperature of transition into smectics.
** Cholesterine γ-Cl-butirate.

the 3 and 4-position of the acyl radical doesn't influence the frequency of the stretching vibrations of the C=O group.

In the PMR spectra of the studied compounds (1–19) in CCl_4 solution the singlet signals appearing at δ = 0.67; 0.82; 0.89 and 1.01 ppm are due to the resonance of the protons of the methyl group in the 18, 25, 26, 21 and 19 positions, respectively, of the alkyl chain. The signal of methylene protons (C_{22}, C_{23}, C_{24}) is observed as a singlet at δ = 1.13 ppm. The signal of the vinyl proton (C_6) was observed as a broad doublet within the range δ = 5.38 ppm.

The signal of protons located in the 3 α-position of the steroid system was observed at δ = 4.93–4.23 ppm as a broad multiplet due to the interaction with the protons of ring A.

In the case of compounds (2, 3) the signal of the protons located at the carbon atom in the α-position bound to halogens is a quadruplet within the range δ = 4.24 and 4.21 ppm, respectively. Protons of the terminal methyl group of the acyl radical give a signal as a doublet at δ = 1.66 (2) and 1.77 ppm (3).

Introduction of halogen into the β-position (compounds 15, 16)

TABLE 5

IR and PMR spectra of α-, β-, γ-halogensubstituted cholesterylalkanoates (XII and XIII)

No	IR spectra, cm^{-1}, tablets with KBr			PMR spectra, δ, ppm in CCl_4				
	ν(C=O)	ν(C—Br)	ν(C—Cl)	$H_{(C_4)}$	$H_{(C_3)}$	$H_{(C_2)}$	$H_{(3\alpha)}$	Vinyl proton
1*	1760		790	—	—	3.91	4.56	5.39
2	1740		820	—	1.66	4.24	4.62	5.4
3	1735	620		—	1.77	4.21	4.5	5.4
4	1740	650		—	2.2	—	4.58	5.38
5	1745		840	not identified		4.06	4.58	5.38
6	1740	620		not identified		4.02	4.58	5.38
7	1735		800	not identified		3.95	4.56	5.39
8	1730	630		—"—	—"—	3.96	4.58	5.38
9	1740		840	—"—	—"—	4.08	4.57	5.38
10	1740	530		—"—	—"—	4.02	4.58	5.42
11	1740	620		—"—	—"—	4.03	4.57	5.4
12	1740		840	—"—	—"—	4.06	4.56	5.38
13	1740		840	—"—	1.3	4.08	4.58	5.38
14	1740	600		—"—	1.38	3.93	4.58	5.4
15	1735		830		3.7	2.72	4.58	5.38
16	1730	590			3.7	2.73	4.6	5.38
17	1740		840	1.57	4.35	3.02	4.58	5.38
18	1730		800	3.6	2.1	2.38	4.56	5.38
19	1730	590		1.79	4.4	3.12	4.58	5.38

* Numbering of compounds corresponds to that in Table 4.

results in the appearance of a proton signal located at the same position as a triplet at δ = 3.7 ppm, and the signal of methylene protons in the α-position—at δ = 2.72 ppm.

In the PMR spectrum of cholesteryl ester of α-bromo-α-methylpropionic acid there is a singlet signal of the protons of the two methyl groups of the acyl radical at δ = 2.2 ppm. (Compound 4 Table 5).

In the case of cholesterine β-Cl-butyrate (17) and cholesterine β-bromobutyrate (19) in their PMR spectra the following signals were found: doublet at δ = 1.57 ppm (17) and 1.79 ppm (19), respectively, belonging to the protons of the terminal methyl group of the acyl radical, two doublets within the range δ = 2.98 and 3.02 ppm (17) and δ = 3.17 and 3.12 ppm (19)—signals of the non-equivalent protons at the α-C atoms. Besides, a multiplet is observed for the proton in the β-position: for compound 17 δ = 4.35 ppm and 4.4 ppm (19).

According to Table 4 introduction of a halogen atom into the vi-

cinity of a carbonyl group influences greatly the mesomorphic properties of the molecules. The presence of the halogen atom in the α-position of the acyl fragment results in the loss of mesogeneity in compounds 1–8. However, with the increase of the hydrocarbon radical length in the 3β-position of the steroid system of rings the effect of the halogen is compensated by the increase of the geometric anisotropy of the molecules and beginning from cholesterine α-Cl-valerate (9) the cholesteric mesophase appears.

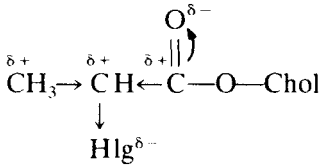
Compounds overcool, i.e., the phase transition isotropic liquid → cholesteric liquid crystal takes place at lower temperature than the transition cholesteric liquid crystals → isotropic liquid. Monotropic smectic mesophase appears alongside with the cholesteric one in the case of cholesterine α-Cl-pelargonate (13). With cholesterine α-bromostearate (14) both cholesteric and smectic mesophases are enantiotropic. Smectic mesophase of compounds 13 and 14 was classified as smectic A.

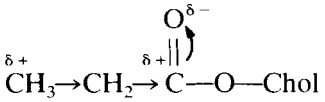
The melting points of the non mesomorphic compounds 1–8 are higher than those of the nonsubstituted cholesterine alkanoates (Table 1) which proves the higher level of organization of the crystalline structure of the former ones and the increase of the intermolecular interaction. At the same time, higher homologues 9–14 exist in mesophase and transform into isotropic liquids at lower temperatures than their unsubstituted analogues. It should be noted that smectics appear much sooner (at the 7th homologue) within the homologous series of unsubstituted cholesterylalkanoates. With the presence of halogen in the α-position smectic mesophase is observed in compounds with nine carbon atoms in the acyl radical.

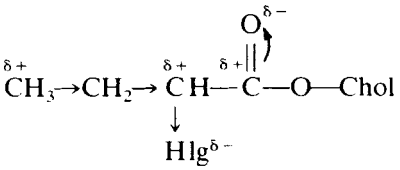
Unlike cholesterine α-halogenalkanoates, esters of cholesterine and β-halogenalkane acids (15–19) form enantiotropic cholesteric mesophase within a rather wide temperature range. All cholesterine β-halogenalkanoates can overcool. The temperature interval of cholesteric mesophase is broadened by overcooling and also by the increase of the transition temperature to the isotropic liquid. With the displacement of the halogen into the γ-position of the acyl chain the enantiotropic cholesteric mesophase is still observed which may be illustrated by compound 18.

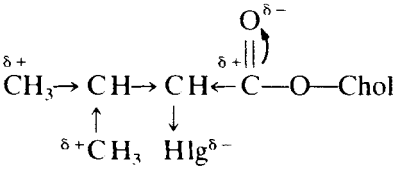
The absence of mesogeneity in compounds with the short acyl radical and the halogen atom in the α-position may be explained by the fact that in this case introduction of the halogen results in the strengthening of side molecular interactions as compared with unsubstituted analogues, since besides carbonyl group an additional

polar group appears which causes the following distribution of the electron density in the molecules:









The partial positive charge on the carbon atom of the carbonyl group of these compounds is larger than that of the unsubstituted cholesterylalkanoates which is due to the electronoacceptor effect of the halogen which also promotes the increase of the side intermolecular interactions.[93]

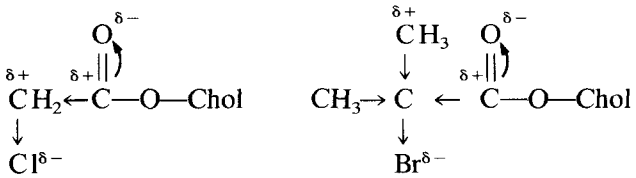
The combined inductive effect of the halogen and the terminal methyl group results in the increase of the partial positive charge on the carbon atom of the terminal methyl group. Hence, terminal intermolecular interactions in the above compounds also increase as compared with unsubstituted analogues. The forces of intermolecular interaction in the crystalline state increase which is proved by the increase of the melting point, thus, it will be difficult for the molecules to preserve the liquid crystalline order. The melting points of unsubstituted cholesterine α-halogenalkanoates are higher by 10–45°C than those of the unsubstituted analogues.[15] High molecular polarizability due to the presence of halogen also promotes the increase of the melting points.

A halogen near a carbonyl group contributes greatly to the perpendicular component of the polarizability ($\alpha_\perp$) while decreasing its parallel component ($\alpha_\parallel$) which depends on the electron density of the

carbonyl group π-bond. As a result, the anisotropy of polarizability ($\Delta\alpha$) of the above compounds decreases. Quantitative calculations are given in Chapter 2.

The decrease of the polarizability anisotropy and the absence of the anisotropy of the forces of intermolecular interactions results, perhaps, in the loss of mesogenic ability by the above compounds.

For compounds 1 and 4, besides the already mentioned factors influencing negatively the mesogenic ability, the disordering of the molecules geometric anisotropy is also observed (i.e., the increase of the width of the molecules owing to the bulky halogen atom or the branching of the alkyl radical). See Table 4.

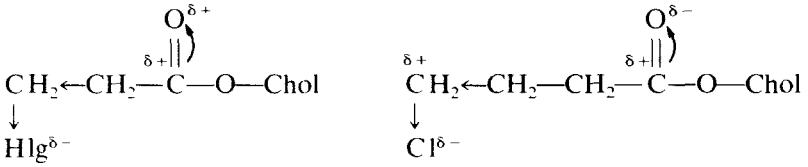


With the increase of the alkyl chain length of cholesterine α-halogenalkanoates the mutual inductive effect of the halogen and the terminal methyl group disappears since inductive effect decreases with the increase of the number of C—C bonds. Besides, owing to the possibility of the formation of "globular" conformations blocking of the electronegative groups by the alkyl chain becomes possible. This results in the weakening of the forces of the intermolecular side interactions and the appearance of cholesteric mesophase at compounds 9–14 containing five and more carbon atoms in the acyl fragment. The temperatures of their transition to the isotropic liquid are lower than those of the unsubstituted analogues[27] by about 40°C which is perhaps due to steric factors weakening the intermolecular interactions between neighbouring molecules.

Further increase of the length of the alkyl radical weakens the terminal interactions of the molecules thus promoting the appearance of smectics, however, steric hindrance due to the large ionic radius of the halogen atom weakens somewhat the side intermolecular interactions, and thus the smectics in the cholesterine α-halogenalkanoates series appear later than in the case of the unsubstituted analogues.

With the presence of the halogen in the β- or γ-position of the short acyl fragment of cholesterine halogenalkanoates the inductive effect of the halogen does not influence the frequency of the stretching

vibrations of the carbonyl bond. This is proved by IR spectra (Table 5), the values of $\nu_{(C=O)}$ for β- and γ-halogenalkanoates of cholesterine do not differ significantly from the $\nu_{(C=O)}$ of the unsubstituted analogues which is 1730 cm^{-1}. Thus, the partial positive charge of the carbon atom of the carbonyl group is identical with that of the unsubstituted cholesterine esters. The side intermolecular interactions are due only to the readily polarizable carbonyl group.

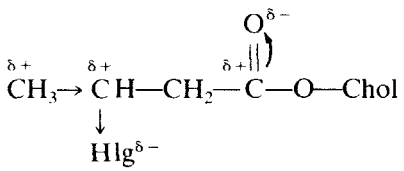


Hlg = Cl, Br

The presence of a halogen atom in the terminal methyl group (compounds 15, 16, 18) increases the terminal intermolecular interactions owing to the enhanced partial positive charge on the carbon atom of the terminal group. PMR spectra (Table 5) indicate that the protons in the β- and γ-position of compounds 15, 16, 18 are descreened more than the protons of terminal methyl groups corresponding to cholesterine α-halogenalkanoates (2, 3, 5, 6). The shift of the proton signal in the weak field is about 2 ppm. Thus, anisotropy of the forces of intermolecular interactions (enhancement of the terminal and weakening of the side interactions) appears.

The presence of a halogen atom in the β- and γ-position increases the parallel component of the molecular polarizability and the anisotropy of the polarizability as compared with cholesterine derivatives containing a halogen in the α-position. The anisotropy of the forces of intermolecular interaction and the increase of the polarizability anisotropy promote the appearance of mesomorphism with cholesterine β- and γ-halogenalkanoates.

In the case of cholesterine β-halogenalkanoates (17, 19) the side interactions between the neighbouring molecules also weaken while the terminal ones are similar to those of the non-mesomorphic compounds 2, 3, 5, 6. The signal of the protons of the terminal methyl groups for compounds 17, 19 is $\delta = 1.57-1.79$ ppm, respectively.



Hlg = Cl, Br

Consequently, anisotropy of the forces of the intermolecular interaction is less than for cholesterine derivatives containing the halogen at the end of the acyl radical; as a result, the temperature range of existence of the cholesteric mesophase for cholesterine β-halogenalkanoates (17, 19) is narrowed (Table 4).

For polar molecules possessing dipole moments, such as cholesterine halogenalkanoates, the contribution of dipole-dipole interaction to the formation of mesomorphic ability increases.

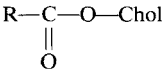
The effect of the constant dipole moment on a compound's mesomorphism is not studied sufficiently and the data on this aspect are contradictory. Some authors[38] consider that geometric anisotropy is a dominating factor determining mesophase stability, and neglect the polarity of compounds. In Ref. 39 the connection is shown of the molecular dipole moment with the transition temperature from the mesomorphic state to the isotropic phase.

We have found experimentally the dipole moments of the above compounds using the second method of Debye for dilute solutions in benzene.[40] For unsubstituted cholesterylalkanoates the μ value was ~1.8–1.9 D, introduction of the halogen caused an increase of the constant dipole moment of the molecules up to 2.2–2.6 D (Table 6). There was no correlation found of the μ values with the mesomorphic properties of the compounds synthesized.

On the basis of the experimental data discussed here it is suggested that the electronic character of the substituent (halogen) is dominating in the formation of mesogenic ability of cholesterine halogenalkanoates with the short acyl fragment, and, beginning from the homologue containing five carbon atoms in the above fragment the steric factor is of special importance.

TABLE 6

Dipole moments of halogensubstituted cholesterylalkanoates

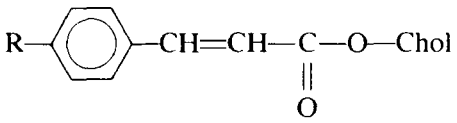


No	*R*	*D*
1	$CH_3CH_2CH_2$—	1.89
2	$CH_3CH_2CH(Br)$—	2.50
3	$CH_3CH(Br)CH_2$—	2.16
4	$CH_3CH_2CH(Cl)$	2.59
5	$CH_3CH(Cl)CH_2$—	2.56
6	$CH_2(Cl)CH_2CH_2$—	2.37
7	$CH_3(CH_2)_6CH(Cl)$—	2.58

1.1.3. Esters of cholesterine and unsaturated carboxylic acids

The presence of multiple bonds within an acyl fragment of the cholesterine ester molecule changes considerably the mesomorphic properties. Conjugation of the double bond with the carbonyl group results in the increase of the phase transition temperatures. The increase of the number of conjugated double bonds results in the intensification of this effect. The configuration of the substituents relative to the double bond is also of importance. The phase transition temperatures of cis-isomers are usually lower than those of the corresponding trans-forms.

The literature data on the esters of cholesterine and unsaturated acids of the aliphatic series are not as numerous as those on similar compounds of the aromatic series.



XIV

R = H, Cl, NO_2, CN, H_2N, OH

In Ref. 4 the phase transition temperatures of some *n*-substituted cholesterine cinnamates are given without interpretations of the effect of substituents on their mesomorphic properties.

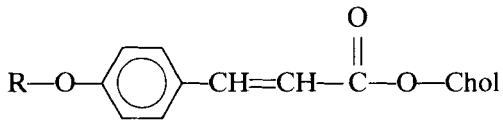
A more detailed study on the systematic series of *n*-substituted cholesterine trans-cinnamates is given in Refs. 5 and 41–43. These authors have carried out a study of the temperature dependence of the helical pitch of cholesterine benzoates and trans-cinnamates; experimental values of the dipole moments were also analyzed, IR spectra of *o*- and *p*-substituted cholesterine benzoates were studied in solutions, in the mesophase and in the crystalline state. It was also shown that *o*-derivatives exist in solution, mesophase and crystals as an equilibrium mixture of rotated isomers differing in the relative position of carbonyl group and *o*-substituent. Besides, by means of X-ray structural analysis and PMR-spectroscopy the preferred conformations of the above compounds were found in the different states of aggregation.

In the work of Dave et al.[44] the synthesis is described of and data are given on the phase transitions of a series of trans-*p*-*n*-alkoxycinnamates of cholesterine (Table 7).

TABLE 7

Mesomorphic characteristics of *p*-*n*-alkoxycholesterylcinnamates (XV)

No	*R*	Temperature of phase transitions, °C			
		T_{sm_1}	T_{sm}	T_{ch}	T_{is}
1	CH_3	—	—	160.5	215.0
2	C_2H_5	—	—	173.0	292.5
3	C_3H_7	—	—	152.0	293.5
4	C_4H_9	—	—	146.0	280.0
5	C_5H_{11}	—	—	134.0	281.0
6	C_6H_{13}	—	—	128.0	268.0
7	C_7H_{15}	—	—	128.5	262.5
8	C_8H_{17}	—	—	142.5	254.0
9	C_9H_{19}	—	—	144.0	249.0
10	$C_{10}H_{21}$	—	—	142.5	244.0
11	$C_{12}H_{25}$	133.0	158.5	167.0	238.5
12	$C_{16}H_{33}$	133.0	178.0	181.5	226.5
13	$C_{18}H_{37}$	—	108.0	167.0	186.0



XV

$R = C_nH_{2n+1}$

$n = 1\text{–}10, 12, 17, 18$

The authors draw an analogy with the saturated cholesteryl-alkanoates. The transition temperatures to the isotropic liquid of the above compounds are higher than those of their analogues of the saturated series.

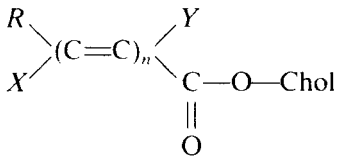
The first nine members of the series form enantiotropic cholesteric mesophase, while higher homologues show polymorphism forming smectic and cholesteric phases. Investigations using polarizing microscopy have shown selective reflection of light.

For the transition temperature of cholesteric mesophase to the isotropic liquid an even-odd effect is observed which consists of the fact that esters with an even number of carbon atoms in the side chain transform to the isotropic state at the higher temperature. Changes in mesomorphic characteristics of the above homologue series as compared with that of the alkoxybenzoates are explained by the presence of the phenyl fragment and the conjugated double bond

which contribute to the geometric anisotropy and the increase of molecular polarizability. The authors suggest that the high polarizability of the molecules increases the transition temperature to the isotropic liquid while the broadening of a molecule owing to the double bond reduces the energy of intermolecular interaction, and hence the smectic mesophase in the homologue series of cholesterine alkoxycinnamates appears much later than in the case of cholesterine alkoxybenzoates.

Thus, literature data on the synthesis and study of the mesomorphic properties of the cholesterine esters containing unsaturated fragment are not sufficient, and the effect of the molecular structure of these compounds on their mesogenic ability is not elucidated. As for the stereochemical aspects of this problem they have been even less studied.

The authors of the present review have synthesized cis-trans-isomeric α, β-substituted acrylic acids and their cholesteryl esters, found some correlation between structure, configuration and conformation of the molecules and their mesomorphic characteristics.[45]



XVI

R = H, CH_3, C_2H_5, C_6H_5, C_4H_3O, C_5H_4N
X = H, CH_3Cl;
Y = H, Br;
n = 1, 2

The synthesis of isomeric crotonic and chlorocrotonic acids was reported previously,[46] as was the synthesis of isomeric unsaturated acids.[47,48] Trans-cinnamic acids were prepared according to the method of Perkin,[49] and cis-cinnamic acid—by the catalytic reduction of phenylpropionic acid,[50] the acid chlorides were prepared by the reaction of the acids with an access of thionyl chloride. Cholesteryl esters were synthesized by the interaction of cholesterine with the corresponding acid chlorides. Identity and purity of the prepared compounds were controlled by thin-layer chromatography on "Silufol-254" plates, with eluent ratio of benzene-cyclohexane 2:1.

The characteristics of the compounds obtained are summarized in Table 8. In Ref. 46 the steric structure of the synthesized acids was proved.

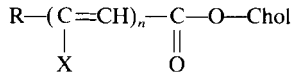
UV spectra were recorded on spectrophotometer "Specord UV-VIS" in ethyl alcohol at the concentration $1-5 \cdot 10^{-6}$ mol/l.

In the UV spectra of cholesteryl esters of isomeric cis-, trans-crotonic acids the intensive band appears at 209 nm due to π-π^*transitions, the larger conjugation in the trans-isomer results in a bathochromic shift of this band as in the initial acids.

Introduction of a benzene ring into a molecule increasing the conjugation chain in the case of cinnamic acid results in a strong bathochromic shift of the main absorption band. However, in the spectrum of cis-cinnamic acid a small hypsochromic shift is observed relative to the trans-isomer band and a considerable reduction of the intensity of the characteristic band. This, on the one hand, proves the cis-configuration of the acid, and on the other, allows one to suggest that molecules of the cholesteric ester of cis-cinnamic acid possess mainly *S*-cis-conformation relative to the central ordinary bond. In the case of cholesteryl esters of trans-cinnamic acid the intensity of the characteristic band is lower than the expected one (as compared with the initial acid) by about 30%. This indicates that an ester mol-

TABLE 8

Cholesteryl esters of β-substituted acrylic acids



No	*R*	*X*	*n*	Configuration	UV spectra ν nm	UV spectra *I*	IR spectra, cm^{-1} ν C=C	IR spectra, cm^{-1} ν C=O	IR spectra, cm^{-1} δ C—H
1	CH_3	H	1	trans	209.5	11080	1630	1692	964
2	CH_3	H	1	cis	206	1750	1640	1706	926
3	CH_3	Cl	1	*Z*	223	11500	1631	1694	1022
4	CH_3	Cl	1	*E*	223	13400	1628	1688	865
5	C_6H_5	H	1	trans	275	21600	1622	1693	964
6	C_6H_5	H	1	cis	260	7200	1638	1708	932
7	CH_3	H	2	α-trans γ-trans	256	16000	1640 1614ave	1696	1016
8	CH_3	H	2	α-cis γ-trans	257	21000	1638 1607ave	1638	980
9	C_6H_5	H	2	α-trans γ-trans	298	37500	1645	1712	990
10	C_6H_5	H	2	α-cis γ-trans	196	30400	1636 1604ave	1698	984

ecule is not perhaps a plane *S*-trans-conformer. The UV spectra of isomeric cholesteryl-β-chlorocrotonate and cholesteryl-β-chloroisocrotonate are almost identical which may indicate the similar conformation of the stereoisomers. The IR spectra also prove the esters' structure.

Analysis of Stuart-Briegleb models has shown that, in molecules of trans-isomers of cholesterine esters and those of the unsaturated esters (1) and (4), the geometric anisotropy of the molecule is not disturbed, and the *S*-cis- and *S*-trans-conformations are equally probable. With the presence of a chlorine atom in the β-position (compound 3) *S*-trans-conformation of the molecule becomes more probable due to the intramolecular dipole interaction of the C—Cl and C=O groups.

Cis-isomers of the studied compounds possess different characteristics. Thus, for cholesterylisocrotonate *S*-cis- and *S*-trans-conformations are equally probable, while with the substitution of the methyl group for a phenyl one the molecule becomes more bulky. Here, the geometric anisotropy of the molecule should be disturbed. In this case, *S*-cis-conformation is more preferable since in this conformation the molecule changes its geometry to a smaller degree.

In cholesteryl-β-chloroisocrotonate (4) the geometry of a molecule is not disturbed, and thus, the *S*-trans- and *S*-cis-conformation are equally probable. However, mesogenic properties of isomers (3) and (4) differ considerably. Since the geometric polarizability of the isomers is practically the same it could be suggested that it is the polarity factor which plays the main role here. The electronic pairs of the halogen atom, the π-bond of the carbonyl group and the π-electrons of the double bond form a localized negative charge which results in the breakdown of the dispersion interaction between the molecules.

Cholesterine esters and esters of unsaturated monocarboxylic acids differ considerably from the esters containing one double bond. The second double bond increases the steric anisotropy of the molecule changing its mesomorphic characteristics. Geometric isomers of cholesterine and unsaturated acids esters differ to a smaller degree than similar compounds containing one double bond. The mesomorphic properties of these compounds were studied using polarizing microscopy. For a quantitative evaluation of the effect of cis-trans isomerism and the nature of substituents in the α- and β-position on the mesomorphic properties, the helical pitch was found and its temperature dependence studied (see Chapter 2.2).

In Table 9 the mesomorphic characteristics of the above compounds are summarized. Unlike the substituted cholesterine alka-

TABLE 9

Mesomorphic characteristics of cholesterylacrylates (XVI)

No	R	X	Y	Z	n	Configuration	T_{ch}, °C	T_{is}, °C	T_{crys}, °C	ΔT, °C
1	H	H	H	O	1		114	140	108	32
2	CH_3	H	H	O	1	trans	112	164	84	80
3	CH_3	H	H	O	1	cis	78	99	69	30
4	C_2H_5	H	H	O	1	trans	66	95	20	75
5	C_6H_5	H	H	O	1	trans	162	200	100	100
6	C_6H_5	H	H	O	1	cis	110	115	65	50
7	CH_3	H	H	O	2	α-trans, γ-trans	129	168	vitrif.	—
8	CH_3	H	H	O	2	α-cis, γ-trans	110	150	vitrif.	—
9	C_6H_5	H	H	O	2	α-trans, γ-trans	147	218	vitrif.	—
10	C_6H_5	H	H	O	2	α-cis, γ-trans	145	215	vitrif.	—
11	CH_3	Cl	H	O	1	*Z*	96	115	104	11
12	CH_3	Cl	H	O	1	*E*	100	112	80	32
13	C_6H_5	CH_3	H	O	1	trans	140	155	115	40
14	H	H	Br	O	1		139	163	102	61
15	C_4H_3O	H	H	O	1	trans	184	201	141	60
16	C_5H_4N	H	H	O	1	trans	130	164	82	82

noates, in which the introduction of substituents into the α-position of the short ester chain may result in the loss of mesogenic properties (Table 4), in the case of the esters of the unsaturated carboxylic acids the above phenomenon is not observed. The presence of a double C=C bond results in the increase of the conjugation along the ester chain of the molecule thus increasing the molecular rigidity and the longitudinal component of the polarizability $\alpha_{\parallel}$. It is known that the transition temperature to the isotropic state varies as $T_{is.} \sim \Delta\alpha^2$, where $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$. The dependence of $T_{is.}$ (mesophase thermostability) on $\Delta\alpha$ can be seen in the case of the above ester series with the introduction of different substituents into the ester chain.

The substitution of a hydrogen atom in the β-position of cholesterine acrylate for phenyl results in the increase of conjugation within the chain contributing additionally to $\alpha_{\parallel}$ due to delocalisation of the π-electrons of the phenyl ring. Cholesterine trans-cinnamate has the largest $T_{is.}$ value as compared with its isomer and other esters. It should be noted that due to the above factors trans-isomers possess higher thermostability than cis-isomers. The methyl group, possessing donor properties, also increases $T_{is.}$ (Cf. cholesterine trans-crotonate and acrylate).

The introduction of a halogen (cholesterine α-Cl-cinnamate, cholesterine β-Cl-crotonate) atom into the α- or β-position instead of hydrogen induces a considerable acceptor effect on the C=C bond decreasing the conjugation in the ester chain and decreasing $T_{is.}$.

In Figure 1 the dependence is given of the temperature interval of existence of the mesophase as ΔT vs. T_{is}. The trans-isomers are more thermostable (line I) than cis-isomers (line II). The linear dependences $\Delta T/T_{is}$ indicate that similar conformers with greater thermostability possess also a wider interval of mesophase existence.

Based on an estimate of the dispersion interaction of mesogenic molecules L. N. Lisetsky et al.[51,52] have shown that most of the orientation order in liquid crystals is provided by the anisotropic part of the dispersion or the induction interaction, and that the steric repulsion gives small corrections only.

The authors of the above work concluded that the energy of the dispersion interaction is linear dependent on the linear moment μ. Since this energy is proportional to the temperature T_{is}, T_{is} must increase with the increase of μ. In our work a number of esters with similar molecular structure were investigated, and it seemed useful to clarify the effect of the μ values on T_{is}. Values of the dipole moments μ were calculated using the SCF method within the CNDO/2 approximation. The cholesterine fragment of the ester molecule

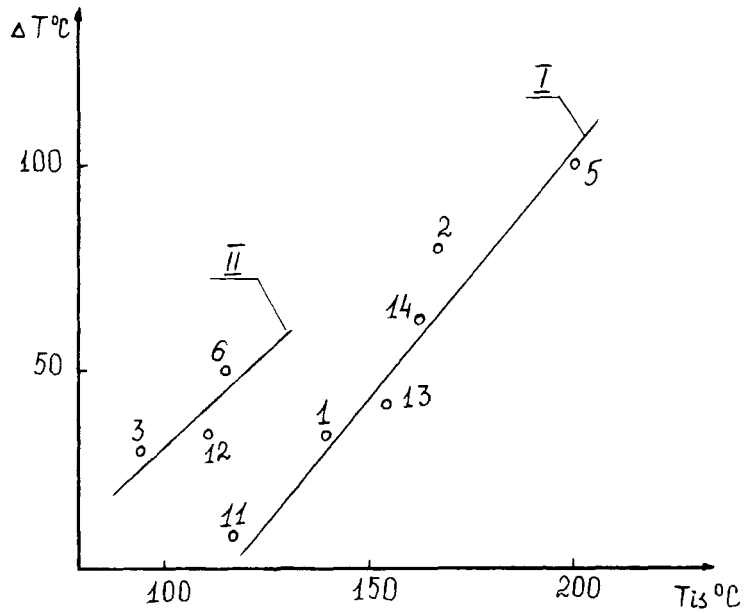


FIGURE 1 Dependence of mesophase existence temperature range on thermostability of cis-trans-isomeric cholesterylalkanoates (numbering of points corresponds to the numbers of the compounds in Table 9).

was modelled by phenyl, so that the μ values given in Table 10 represent the relative change of the studied CLC. When calculating the value of the full dipole moment μ for molecules containing a halogen atom the contribution of the overlap integrals of the wave functions of *s*-, *p*- and *d*-orbitals should be taken into account.

As Table 10 shows the μ values for the trans-isomers are larger than those for the cis-isomers. An increase of the conjugation in the chain results in an increase of the dipole moment value. Substitution of hydrogen for donor groups (CH_3, phenyl) in trans-isomers results in an increase of μ.

The linear dependences of the experimental $T_{is.}$ values on the calculated μ values (Figure 2) testify to the validity of the theory explaining orientation ordering in mesophases mainly by the anisotropic dispersion forces of the interaction.

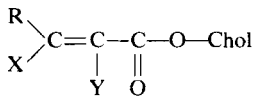
Information on the effect of substituents and isomerism in the class of esters of unsaturated carboxylic acids on their mesomorphic properties is obtained from IR absorption spectra.

IR spectroscopy techniques are rather informative about the liquid crystalline state. Thus, according to the data on the temperature measurement of IR spectra it is possible to determine the interval of mesophase existence. IR spectroscopic study of oriented samples in the region of the characteristic absorption frequencies allows one to identify the molecular structure in a liquid crystal, carry out conformational analysis, determine isomerism and the presence of steric electron effects (resonance, acceptor, conjugation) etc.

IR spectra of the studied CLC classes were measured on the sam-

TABLE 10

Values of the dipole moments and polarizability anisotropy of α-, β-substituted cholesterine acrylates



No	*R*	*X*	*Y*	Configuration	μ_D	$\alpha_{\parallel}$(Å^3)	$\alpha_{\perp}$(Å^3)	$\Delta\alpha$(Å^3)	$\bar{\alpha}$(Å^3)
1	H	H	H	—	2.14	79.58	47.30	32.28	58.06
2	C_6H_5	H	H	trans	3.02	91.57	58.84	32.73	69.75
3	C_6H_5	H	Cl	trans	3.47	94.17	60.66	33.51	71.83
4	CH_3	H	H	trans	2.75	81.87	49.14	32.73	60.05
5	CH_3	H	H	cis	1.26				
6	CH_3	Cl	H	*Z*	2.51	84.47	50.96	33.51	62.13
7	CH_3	Cl	H	*E*	1.55				

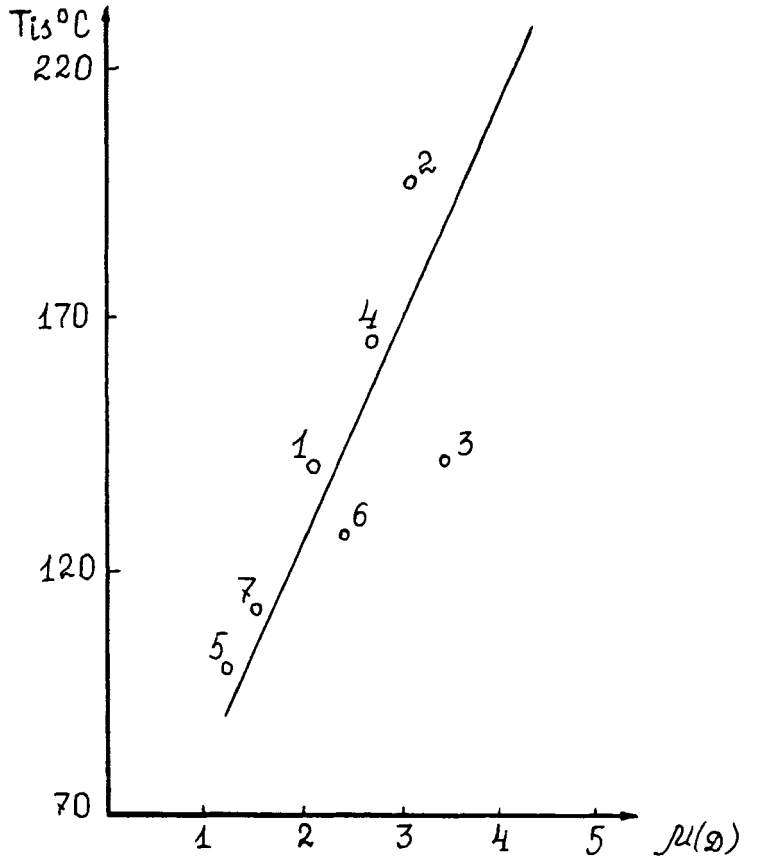


FIGURE 2 Dependence of cholesterylacrylates thermostability on the calculated value of the dipole moment.

1—cholesterylacrylate;
2—cholesterylcinnamate (trans);
3—cholesterylchlorocinnamate (trans);
4—cholesterylcrotonate;
5—cholesterylcrotonate (cis);
6—cholesterylchlorocrotonate (*Z*);
7—cholesterylisochlorocrotonate (*E*).

ples of the thickness ~15 μm, oriented by polishing the KBr plates. The spectrum was recorded on spectrophotometer "Specord 75 IR" with sample temperature controlled to an accuracy of 0.2°.

The positions of the frequencies and the intensities in the IR spectra were correlated with the values of the electron density at atoms and group of atoms, orders of bonds, and molecular energies resulting from quantum-chemical calculations. This allowed one to estimate

the degree of approximation in the model structures of the studied molecules to the real ones. A detailed comparison of the quantum chemical calculations with the data of the IR spectra is given below.

In Table 11 the most characteristic frequency bands are given in IR spectra for unsubstituted and substituted cholesterine acrylates recorded in mesophase. The investigations indicated that bands characterizing isomerism and the type of substituents are connected with the stretching vibrations of the carbonyl group C=O ($\nu_{C=C}$), vibrations of C=C ($\nu_{C=C}$) and conjugation of the C=C bond with the C=O one. The table indicates that in the spectra of acrylates trans-isomers and those of substituted cholesterine acrylates the band $\nu_{C=O}$ is situated at 1713 cm^{-1} while in the spectra of their cis-isomers— $\nu_{C=O}$ = 1734 cm^{-1}. For the pure isomers this band is single; sometimes there is a weak shoulder (for example, in the case of crotonates) indicating the presence of some amount of one isomer within another. In Table 9 the values of the frequencies of the most intensive peaks characteristic of the isomers are given.

The absorption band due to the vibrations of the C=C bond is also sensitive to the type of isomers and substituents. In the spectra of cholesterine acrylates there are practically no $\nu_{C=C}$ bands observed. Upon the introduction of a methyl group or a benzene ring as the substituents into the β-position there appear intensive bands of the C=C bond vibrations. These bands in trans-isomers are shifted towards the long wave length region as compared with the same bands in the cis-isomers. The long wave length shift is due to the increase of the length of the C=C bond caused by the increase in conjugation in the chain of the molecules of the trans-isomers. In the case of cholesterine cis-cinnamate the bands of the C=C bond vibrations possess low intensity which is due to the decrease in conjugation in this form.

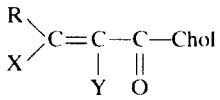
For trans-isomers a new absorption band appears in the spectrum at ν = 1580 cm^{-1} due to conjugation of the C=C bond with the C=O one. In the case of β-Cl-crotonate (cis) there is no band $\nu_{\text{conj}\{C=O}^{C=C}$ observed which is due to the decrease of conjugation owing to the acceptor effect of the chlorine atom.

Besides the above frequencies there is a set of frequencies in the IR spectrum characterizing the type of substituents. Thus, introduction of a benzene ring into the β-position of trans-isomers results in the increase of the number of bands due to the CH_2-vibrations: there both scissoring and wagging vibrations are observed. Bands due to CH_3-vibrations change their intensity for different isomers but the frequency of their vibrations is the same.

Quantum-chemical calculations show (Table 11) that a decrease of

TABLE 11

Electronic characteristics of the molecules and the characteristic frequencies of the IR spectra



No	*R*	*Y*	*X*	Configuration	E_{tot}	δ(C_1)	δ(O)	δ(C_2)	ν(C_3)	$\nu_{C=O}^{cm^{-1}}$	$\nu_{C=C}^{cm^{-1}}$	$\nu_{comj}^{cm^{-1}}$
1	H	H	H	—	−2902.35	0.388	−0.377	−0.056	0.021	1734	1674 1640	
2	C_6H_5	H	H	trans	−4145.85	0.384	−0.374	−0.085	0.060	1713	1640 1640	1580
3	C_6H_5	H	H	cis						1734	1607 1667 1613	
4	C_6H_5	Cl	H	trans	−4564.49	0.384	−0.330	−0.001	0.058	1713	1634	1580
5	CH_3	H	H	trans	−3132.57	0.403	−0.381	−0.242	0.308	1713	1600	1580
6	CH_3	H	H	cis	−3132.43	0.399	−0.372	−0.247	0.311	1734	1640	
7	CH_3	H	Cl	*Z*	−3552.32	0.406	−0.374	−0.225	0.346	1713	1634 1667	
8	CH_3	H	Cl	*E*	−3551.9	0.398	−0.360	−0.229	0.353	1734 1687	1640 1634	

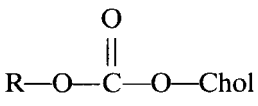
the electron density of two neighbouring atoms results in an increase of the bond length, decrease of the bond order and a reduction of the frequency of the stretching vibrations.

Calculations of the values of the full electron energies E_{full} for mesogenic molecules indicate that trans-isomers are more stable than cis-isomers. Introduction of substituents results in the stabilization of the molecular structure.

Thus, the structure of the IR spectra reveals isomerism and the type of substituents in the above series of mesogenic molecules and it is satisfactorily described by quantum-chemical calculations. The structure of the molecules as well as their electronic properties determine the macroscopic characteristics of the mesophase: Thermostability, interval of mesophase existence etc.

1.1.4. Cholesterylalkyl- and cholesterylarylcarbonates

Cholesterylalkyl- and cholesterylarylcarbonates are insufficiently described. Only the saturated cholesterylalkylcarbonates are described,[53] as well as some members of the unsaturated and aromatic series.[54]



XVII

$R = C_nH_{2n+1}$

$n = 1-22$

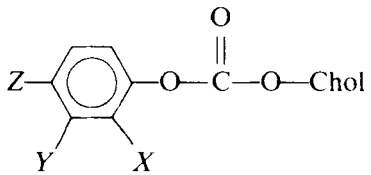
Synthesis is reported in Ref. 53. Cholesterylalkylcarbonates were prepared by the condensation of cholesterylchloroformate with the corresponding alcohols in the medium of absolute ester in the presence of pyridine. Mesomorphic characteristics are given in Table 12. Elser et al. have carried out a study on the effect of the structure of these compounds on their mesomorphism and given comparative characteristics of cholesterylalkylcarbonates and cholesterylalkanoates. They have also found a clear tendency for a decrease of thermostability ($T_{is.}$) of the mesophase and an increase of number of monotropic cholesteric mesomorphogens. The authors suggest that both facts prove the disturbance of the geometric anisotropy of cholesterylalkylcarbonate molecules, though it is difficult to explain this disturbance, since substitution of a carbon atom for an oxygen one should not be significant due to the approximate identity of their valence angles. There is probably another reason for the change of mesophase thermostability.

TABLE 12

Mesomorphic characteristics of cholesterylalkylcarbonates (XVII)

No	*R*	Temperature of phase transitions, °C		
		T_{sm}	T_{ch}	T_{is}
1	CH_3		(110.9)	114
2	C_2H_5		83.9	105.8
3	C_3H_7		98.8	101.0
4	C_4H_9		80.2	94.0
5	C_5H_{11}			106.3
6	C_6H_{13}			108.3
7	C_7H_{15}		(81.3)	88.0
8	C_8H_{17}	(35.4)	54.8	78.9
9	C_9H_{19}	(45.1	77.2)	79.3
10	$C_{10}H_{21}$	(48.7	75.9)	76.6
11	$C_{11}H_{23}$	(51.1)	70.5	74.4
12	$C_{12}H_{25}$	(51.7)	61.7	72.9
13	$C_{13}H_{27}$	(52.1)	61.9	71.3
14	$C_{14}H_{29}$	(52.9)	68.7	70.4
15	$C_{15}H_{31}$	(53.9)	69.0	69.7
16	$C_{16}H_{33}$	(54.9	69.2)	73.9
17	$C_{17}H_{35}$	(55.5	68.6)	74.1
18	$C_{18}H_{37}$	(55.6	67.7)	78.2
19	$C_{19}H_{39}$		(67.1)	78.7
20	$C_{20}H_{41}$		(65.9)	80.9
21	$C_{22}H_{45}$		70	81

Authors of the present paper have synthesized and studied the mesomorphic properties of substituted cholesterylphenylcarbonates.[55,56]



XVIII

X = CH_3, C_2H_5, F, Cl, Br, NO_2
Y = CH_3, C_2H_5, Cl, NO_2
Z = CH_3, F, Cl, Br, NO_2

Synthesis was accomplished according to Ref. 55 via the stage of cholesterylchlorocarbonate preparation followed by reaction with the corresponding phenols.

Purification of the synthesized compounds was carried out by repeated recrystallization and column chromatography. Identity of the compounds was proven by thin layer chromatography. Composition and structure were proven by microanalysis and IR spectroscopy. Mesophase intervals and textures of the studied compounds were determined on the polarizing microscope "Полам-P-312" with thermal device. The results are summarized in Table 13.

Both cholesterylphenylcarbonates and cholesterine benzoates[57] illustrate the effect of the stereochemical and electronic properties of the molecules on the mesomorphic characteristics of the cholesteric phase. Owing to the presence of the C—O—C bond between the benzene ring and the carbonyl group, the structure of phenylcholesterylcarbonate becomes more rigid than in the case of benzoates which results in a more "loose" packing of the molecules ($r_{\text{eff.}}$ increases) and in a decrease of the energy of the intermolecular interaction which in turn results in a decrease of the mesophase thermostability.

As Table 13 shows, introduction of a halogen (F, Cl, Br) and a nitro group into the ortho-position of the benzene ring changes somewhat the mesophase thermostability ($T_{\text{is.}}$) while introduction of a

TABLE 13

Mesomorphic characteristics of substituted cholesterylphenylcarbonates (XVIII)

No	X	Y	Z	Temperature of phase transitions, °C	
				$T_{\text{chol.}}$	T_{is}
1	—	—	—	45	120
2		—	—	(97)	127
3	Cl	—	—	(*)	122
4	Br	—	—	(*)	102
5	NO_2	—	—	(68)	124
6	CH_3	—	—	128	157
7	C_2H_5	—	—	169	218
8	—	Cl	—	(77)	106
9	—	NO_2	—	(*)	131
10	—	CH_3	—	(114)	125
11	—	C_2H_5	—	117	135
12	—	—		141 (122)	151
13	—	—	Cl	(*)	120
14	—	—	Br	146	153
15	—	—	NO_2	164	210
16	—	—	CH_3	131	145

* Crystallization is observed at room temperature.

methyl or an ethyl group increases $T_{is.}$. Introduction of substituents (NO_2, Br) into the para-position results in the largest increase of $T_{is.}$.

The dependence of $T_{is.}$ on the type and position of the substituents in the benzene ring indicates the determining role of the molecular dipole moment in mesophase formation. Thus, introduction of halogen atoms into the ortho-position of the benzene ring results in a decrease of the electron density in the ring with an increase of the acceptor ability of the substituents within the series F > Cl > Br; as a consequence, the dipole moment of the ring increases, thus increasing the dipole moment of the molecule μ. Similar effects are observed with the substitution of a hydrogen atom for a donor group in the benzene ring. Introduction of substituents into the para-position, as compared with the ortho-position, increases considerably the dipole moment μ and $T_{is.}$ (Cf. NO_2, Br-ortho and NO_2-para, Br-parasubstituted).

In order to clarify the effect of substituents on the stereochemical and electronic properties of the above class of mesogenic molecules, IR absorption spectra were studied in the solid state, the mesophase and in the isotropic liquid. Characteristic frequencies of the vibrations of substituted phenylcholesterylcarbonates in mesophase are given in Table 14.

Unlike in other classes of steroid derivatives, the characteristic spectrum of IR absorption of phenylcholesterylcarbonates is determined by the rotation of the benzene ring around the C—O bond (alteration of φ angle) which results in the formation of conformers showing the splitting of vibration band $\nu_{C=O}$, ν_{O-C-O} which was also reported in Ref. 58. An investigation of the size of the potential barriers resulting from conformational analysis shows that, due to the small size of these barriers (for carbonyl group $\Delta E \sim 5$ kcal/mol), the conformers are readily transformed from one to another. With the introduction of small substituents into the ortho-position of the benzene ring the splitting of the frequency $\nu_{O-C-O} \sim 30$ cm^{-1} is observed and in the case of bulky substituents (Br, NO_2, CH_3, C_2H_5) this splitting increases up to 40–70 cm^{-1}, and the splitting of the frequency $\nu_{C=O}$ appears. Evidently, introduction of substituents into the ortho-position of the benzene ring results in the formation of conformers with different orientation of the carbonyl group in space.

Investigation of the temperature dependence of the form of the ν_{O-C-O} band shows that in the solid state the long wave length component possesses much lower intensity than the short wave one, in mesophase the intensities of the components are about the same and in the isotropic liquid the short wave peak practically disappears.

This agrees with our suggestion that steric effects between substituents and the carbonyl group yield two conformers located in different basis planes which results in the formation of a layer structure even in the solid state thus causing the formation of cholesterine mesophase.

As shown in Table 14, in the series of halogensubstituted cholesterine benzoates the ν_{Ph} band for ortho-fluorophenylcholesteryl carbonate possesses the highest intensity, while the ortho-Br-substituted one the lowest. The dipole moment of the benzene ring depends on the substituent type: since fluorine possesses the largest acceptor ability it increases most the dipole moment. In the spectrum of ortho-Br and para-Br-phenylcholesterylcarbonate there is no ν_{Ph} band. The donor substituents CH_3, C_2H_5, NO_2 modify noticeably the dipole moment of the benzene ring, the nitro-group in particular, since it increases the intensity of the ν_{Ph} bands and leads to the splitting of the ν_{Ph} band for asymmetric vibrations.

The steric influence of substituents on the frequency of the carbonyl group $\nu_{C=O}$ vibrations proves less noticeable than in the case of the ν_{O-C-O} vibrations: acceptor substituents increase the $\nu_{C=O}$ value by 10 cm^{-1}, while the donor ones decrease it in general by 3–10 cm^{-1}.

Thus, within the above considered class of substituted phenylcholesterylcarbonates the mesomorphic properties are mainly influenced by polar and steric effects. The former determine the energy of intermolecular inductive interactions thus determining the mesophase thermostability. The steric effects of substituents interacting with the carbonyl group are responsible for conformer formation and cause the layer structure forming the cholesteric mesophase. The results on the temperature dependence of the helical pitch in substituted phenylcholesterylcarbonates are given in Chapter 2.

1.2. Thiocholesterine derivatives

Thiocholesterine, unlike its oxygen containing analogue possesses mesogenic ability.[59] It is characterized by the right twisting of the cholesteric helix which is also observed with cholesterine halogenides.[60]

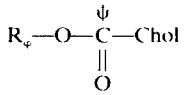
Thiocholesterine was at first synthesized in 1926 according to the procedure described in Ref. 61, and later according to Ref. 62.

1.2.1. Esters of thiocholesterine and saturated carboxylic acids

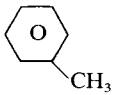
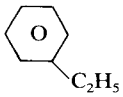
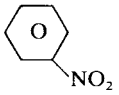
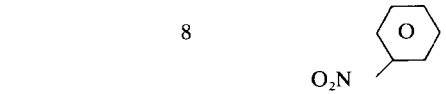
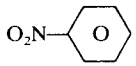
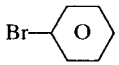
Substitution of an ester oxygen atom in the ester group for a sulphur in cholesterine derivatives results in considerable changes of their mesomorphic characteristics. This fact can be explained by the change

TABLE 14

Characteristic frequencies of the IR absorption spectra



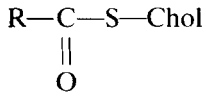
No	*R*	$\nu_{C=O}$(cm^{-1})	ν_{Ph}(cm^{-1})	ν_{O-C-O}(cm^{-1})	ν_{C-NO_2}(cm^{-1})
1		1747	1580 1480	1200	
2		1757	1580 1480	1243 1173	
3		1750	1557 (weak) 1470 (weak)	1240 1210	
4		1750	— —	1270 1207	

5		1740	1593, 1567 (weak) 1480 (weak)	1240 1213	
6		1730	— —	1257 1233	
7		1760, 1730	1593 1580	1260 1240 1207	1520 1333
8		1740	1587 1480	1253 1213	1520 1340
9		1757 1750	1603, 1586 1487	1200 1247	1520 1333
10		1756	— —	1250 1220	

in configuration of the thiocholesterine derivative molecules due to the larger radius of the sulphur atom and the increase of the slope of the axis of *n*-alkyl radical towards the steroid system plane.[63]

In Refs. 64 and 65 the synthesis of thiocholesterylbenzoates is described which were prepared by the reaction of benzoyl chloride with thiocholesterine in pyridine medium. However, this method gave low yields and demanded repeated recrystallization of the reaction products.

Elser and Pohlmann have synthesized a number of thiocholesterine alkanoates by the reaction of thiocholesterine with the corresponding alkancarboxylic acids in the presence of 1,1-carbonyldiimidazole 20.



XIX

$R = C_nH_{2n+1}$
$n = 0–20$

This procedure gave yields of 60–93%. The mesomorphic characteristics are summarized in Table 15. Monotropic cholesteric meso-

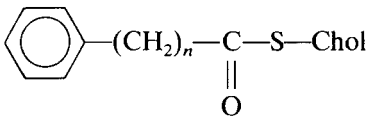
TABLE 15

Mesomorphic characteristics of thiocholesterylalkanoates (XIX)

No	*R*	Temperature of phase transitions, °C		
		T_{sm}	T_{ch}	T_{is}
1	H	—	—	118.3
2	CH_3	—	(119.5)	126.2
3	C_2H_5	—	(111.1)	111.4
4	C_3H_7	—	100.6	117.6
5	C_4H_9	—	90.7	104.7
6	C_5H_{11}	—	94.8	107.7
7	C_6H_{13}	(73.1)	(102.1)	107.0
8	C_7H_{15}	(76.6)	97.3	100.8
9	C_8H_{17}	68.2	84.0	97.5
10	C_9H_{19}	69.5	87.4	98.3
11	$C_{10}H_{21}$	80.5	88.1	95.0
12	$C_{11}H_{23}$	83.5	86.7	92.3
13	$C_{12}H_{25}$	78.9	86.5	91.4
14	$C_{13}H_{27}$	72.2	85.5	90.4
15	$C_{14}H_{29}$	61.3	84.3	88.3
16	$C_{15}H_{31}$	57.0	83.0	87.3
17	$C_{16}H_{33}$	67.5	81.2	85.0
18	$C_{17}H_{35}$	64.5	80.2	84.2
19	$C_{18}H_{37}$	73.5	78.3	82.4
20	$C_{19}H_{39}$	71.2	77.1	81.3

phase was detected for all the members of this homologous series except the 1st one. Selective reflection of light is observed from the 5th to the 8th homologue inclusive. Thiocholesterine caprilate and the next homologues display also monotropic smectic mesophase. Comparison of the mesomorphic properties of compounds of the XIX series (Table 15) with the oxygen containing analogues (I) (Table 1) suggests that substitution of an ester oxygen in the carboxy-group for sulphur increases, in general, the temperature of both the smectic-cholesteric and cholesteric-isotropic transitions.[20,66] Some members of the XIX series are characterized by high thermosensitivity (cholesteric mesophase interval—0.3°) which is important for practical applications.

Introduction of the phenyl radical into the ω-position of the acyl part of cholesterine alkanoate molecules and investigation of the mesomorphism of the so obtained thiocholesterine ω-phenylalkanoates were carried out in Ref. 26.



$n = 0–7$

Comparing the homologous series XIX and XX (Tables 15 and 16, respectively) it can be concluded that introduction of the phenyl fragment into the ω-position increases the phase transition temperatures of the first four homologues of the XX series which are enantiotropic cholesteric liquid crystals. Removal of the phenyl group

TABLE 16

Mesomorphic characteristics of thiocholesterine ω-phenylalkanoates (XX)

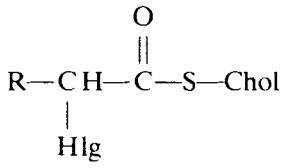
No	n	Temperature of phase transitions, °C	
		T_{chol}	T_{is}
1	0	167	196
2	1	—	125
3	2	135	148
4	3	—	98
5	4	105	107
6	5	—	82
7	6	(94)	95
8	7	(35)	70

from the carbonyl group results in the decrease of the phase transition temperatures and transformation of the enantiotropic cholesteric mesophase into the monotropic one.

1.2.2. Esters of thiocholesterine and halogensubstituted carboxylic acids

Synthesis and properties of the halogensubstituted thiocholesterine alkanoates are described in Refs. 67–69.

When the synthesis of thiocholesterine esters was carried out according to the method based on the preparation of their oxygen analogues the yields of thiocholesterine α-halogenalkanoates reached 15%. Using triethylamine instead of pyridine increased the yield of the final products up to 75%. Thiocholesterine α-halogenalkanoates were prepared by condensation of the corresponding α-halogensubstituted saturated carboxylic acid chlorides with thiocholesterine in a non-polar solvent in an inert gas atmosphere and in the presence of triethylamine.



$R = C_nH_{2n+1}$
$n = 1, 5, 7–16$

Purification of the synthesized compounds was carried out by column chromatography (silica gel L 100/400, eluent-hexane). Their composition was proved by microanalysis, and their structure by IR and PMR spectroscopy. Spectral characteristics are given in Table 18, and their mesomorphic properties in Table 17.

Thus, in the IR spectra of the synthesized thiocholesterine α-halogenalkanoates a band is present within the region 1690–1660 cm^{-1} characteristic of the vibrations of the carbonyl group in thioesters.

Presence of a halogen is proved by the absorption bands in the region 850–820 cm^{-1} (ν_{C-Cl}) and 650–640 cm^{-1} (ν_{C-Br}). Bands in the region 960–880 cm^{-1} correspond to the stretching vibrations of the C—S bond.

Substitution of an ester oxygen for sulphur results in considerable reduction of the $\nu_{C=O}$ (up to 60 cm^{-1}) in thioesters (1–13) as compared with their oxygen containing analogues (Table 4).

In the PMR spectra of α-halogensubstituted thiocholesterine alkanoates the signal of a proton situated in the 3α-position of the

TABLE 17

Mesomorphic characteristics of thiocholesterine α-halogenalkanoates (XXI)

No	R	Hlg	Temperature of phase transition, °C			
			$T_{cryst.}$	T_{sm}	T_{ch}	T_{is}
1	CH_3	Cl	(74)	—	(75.0)	90.0
2	CH_3	Br		—	(77.0)	92.0
3	$(CH_3)_2$	Br	—	—	—	153.0
4	CH_3CH_2	Cl	(30)	—	(31.0)	87.0
5	CH_3CH_2	Br	(35)	—	(40.0)	79.6
6	$(CH_3)_2CH$	Cl	(72)	—	(82.0)	105.6
7	$(CH_3)_2CH$	Br	(89)	—	(95.0)	121.0
8	$CH_3(CH_2)_2$	Cl	(27)	—	(29.5)	95.0
9	$CH_3(CH_2)_2$	Br	(25)	—	(31)	77.4
10	$CH_3(CH_2)_3$	Br	(27)	—	(30.0)	65.0
11	$CH_3(CH_2)_4$	Cl	(36.5)	—	(40.0)	88.0
12	$CH_3(CH_2)_6$	Cl	room	(36.0)	(45.0)	51.0
13	$CH_3(CH_2)_{15}$	Br	—	—	—	44.0

TABLE 18

Spectral characteristics of thiocholesterine α-halogenalkanoates (XXI)

No	IR spectra, cm^{-1}, tablets with KBr			PMR-spectra, δ, ppm in CCl_4			
	ν(C=O)	ν(C—Br)	ν(C—Cl)	$H(C_{3'})$	$H(C_{2'})$	H(3α)	Vinyl proton
1	1690		820	1.7	4.32	3.26	5.38
2	1690	650		1.83	4.4	3.28	5.3
3	1690	650	—	2.36	—	3.16	5.36
4	1660		820	not identified	4.22	3.28	5.38
5	1660	650		—"—	4.18	3.3	5.38
6	1660		840	—"—	4.08	3.26	5.36
7	1660	645		—"—	4.08	3.26	5.36
8	1660		850	—"—	4.18	3.26	5.36
9	1660	650		—"—	4.20	3.26	5.38
10	1660	640		—"—	4.19	3.26	5.36
11	1690		845	—"—	4.2	3.28	5.38
12	1660		840	1.38	4.2	3.26	5.38
13	1700	630	—	1.38	4.19	3.26	5.39

Numbering of the compounds corresponds to that in Table 17.

cyclopentanperhydrophenanthrene fragment shows up in the region δ = 3.26–3.3 ppm. The signal of the proton located at C_2 represents a quadruplet within the region δ = 4.08–4.4 ppm.

Comparison of the PMR spectra of cholesterine α-halogenalkanoates (Table 5) and their thioanalogues (Table 18) indicates that

in the spectra of the latter a shift is observed towards the strong field of the 3α-proton signal approximately by $\delta = 1.3$ ppm, and a shift towards the weak field ~ by $\delta = 0.16$ ppm of the proton signal in the C_2-position. These data indicate that the 3α-proton of the cyclopentanperhydrophenanthrene fragment in the synthesized thioesters is the more screened one.

Study of the mesomorphism of compounds (1–13) was carried out by polarizing microscopy, the data obtained are summarized in Table 17.

The main difference in the mesomorphic properties of α-halogen-substituted thiocholesterine alkanoates, as compared with unsubstituted thioanalogues,[15] consists of a decrease of the temperatures of transition II → CLC and the range of mesophase existence. Besides, synthesized thiocholesterine derivatives are monotropic.

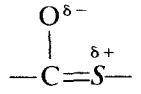
Comparing the mesomorphism of cholesterine α-halogen-alkanoates and their thioanalogues the following differences can be seen:

a. the first members of the homologous series of α-halogensubstituted thiocholesterine alkanoates possess mesogeneity, while their oxygen containing analogues do not;

b. all the members of the homologous series of thioesters in cholesteric mesophase do not show selective reflection of light within the visible part of the spectrum.

Changes in the mesomorphic properties of synthesized thioesters are probably due to the following: the electronegativity of sulphur is less than that of oxygen which results in the decrease of $\nu_{C=O}$ by about 60 cm^{-1} and in the shift towards the strong field by $\delta = 1.3$ ppm of the 3α-proton signal.

In Ref. 20 it was reported that the absorption band of the C=O bond for unsubstituted thiocholesterylalkanoates was 1680–1670 cm^{-1}, in Ref. 70—1690 cm^{-1}, consequently, the inductive effect of the halogen located near the carbonyl group doesn't influence the frequency of its vibrations, since $\nu_{C=O}$ of thiocholesterine α-halogen-alkanoates doesn't differ from the values for unsubstituted thioanalogues. Evidently, in this case the resonance effect is predominant

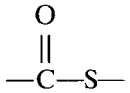


which increases the length of the carbonyl bond reducing $\nu_{C=O}$.[71]

It should be noted that the radius of the sulphur atom is twice as large as that of the oxygen atom and, as it is reported in Ref. 63 the

angle of the C—O—C bond is 110°, while the length of the C—O bond is 1.3 Å, the angle of the C—S—C bond is 104°, and the length of the C—S bond is 1.7 Å. This promotes the increase of the distance between the carbonyl group and the cyclopentanperhydrophenanthrene fragment. It is known[72] that the angle of the slope of the *n*-alkyl radical axis towards the plane of the steroid system for thiocholesterylalkanoates is 15°, for their oxygen analogues—5°. The absence of selective reflection of light of thiocholesterine α-halogenalkanoates is probably due to the acoplanarity of the acyl fragment and the steroid system and the impossibility of forming a planar texture.

The side intermolecular interactions between the fragments



are strong which, according to Gray, should result in smectic mesomorphism. However, the presence of the bulky halogen atom weakens the side attraction, so that in thiocholesterine α-halogenalkanoates the less ordered cholesteric mesophase is observed rather than the smectic one.

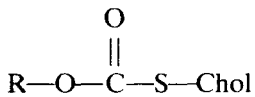
Substitution of an ester oxygen in a carboxy-group for sulphur results in a decrease of the dipole moment of thiocholesterine α-halogenalkanoates by ~0.2 D. This indicates no substantial change of the dipole-dipole interaction. The low thermal stability and the narrow interval of the mesophase existence of thiocholesterine α-halogenalkanoates may be due to the decrease of the polarizability ($\Delta\alpha$) anisotropy of the above compounds since substitution of oxygen for the less electronegative sulphur decreases the component of polarizability along the long molecular axis ($\alpha_{\parallel}$).

Disturbance of the geometric anisotropy as, for example, for thiocholesterine α-Br-isobutyrate (3) results in the absence of mesogenic properties.

The attempt to prepare thiocholesterine β-halogenalkanoates via the reaction of the corresponding acid chlorides with thiocholesterine yielded compounds with no halogen in their composition. In the IR spectra of the compounds obtained recorded in CCl_4 solution the absorption band of the C=O bond was observed at 1670–1660 cm^{-1}, characteristic for thioesters. Using mass spectrometry we have shown that alongside with the reaction of nucleophilic addition to carbonyl group the reaction of nucleophilic substitution of carbon atom bound to halogen takes place in the thiocholesteryl fragment.

1.2.3. Thiocholesterylalkyl- and Thiocholesterylarylcarbonates

Going from cholesterylalkylcarbonates to their thioanalogues is accompanied by a change in the phase transition temperature and mesophase existence interval. In Refs. 73 and 74 the data are given on mesomorphic properties of different cholesterylalkylcarbonates containing sulphur including thiocholesterylalkylcarbonates.



XXII

$R = C_nH_{2n+1}$
$n = 1-20$

In comparing the transition temperatures of cholesterylalkylcarbonates (Table 13) and thiocholesterylalkylcarbonates (Table 19) to the isotropic state an increase of the thermal stability of thiocholesterine carbonates is observed. The authors of these investigations failed to explain the observed experimental data.

They suggest that electronic and structural effects must really pro-

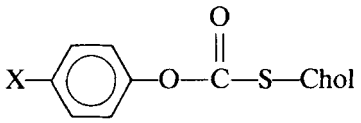
TABLE 19

Mesomorphic characteristics of thiocholesterylalkylcarbonates (XXII)

No	R	Temperature of phase transitions, °C		
		T_{sm}	T_{chol}	T_{is}
1	CH_3	—	(111)	126
2	C_2H_5	—	(108)	131
3	C_3H_7	—	(96)	108
4	C_4H_9	(30)	(95)	101
5	C_5H_{11}	(58)	(91)	94
6	C_6H_{13}	(67)	(94)	91
7	C_7H_{15}	(63)	(83)	93
8	C_8H_{17}	(65)	(83)	89
9	C_9H_{19}	(71)	72	85
10	$C_{10}H_{21}$	(71)	78	84
11	$C_{11}H_{23}$	(71)	(81)	88
12	$C_{12}H_{25}$	(70)	(81)	93
13	$C_{13}H_{27}$	(68)	(78)	80
14	$C_{14}H_{29}$	(67)	(77)	79
15	$C_{15}H_{31}$	(66)	(76)	84
16	$C_{16}H_{33}$	(65)	(75)	83
17	$C_{17}H_{35}$	(64)	71	75
18	$C_{18}H_{37}$	(63)	64	73
19	$C_{19}H_{39}$	(62)	(71)	75
20	$C_{20}H_{41}$	(61)	70	71

mote the transition of electrons from the C=O bond towards the sulphur atom thus promoting the decrease of the C=O bond strength and an increase of the C—S bond. Similar effects should result in a decrease of the thermostability of the smectic phase, i.e., in contrast to that observed in practice.

Thiocholesterylarylcarbonates of the common formula



XXIII

X = H, CH_3, C_8H_{17}, $C(CH_3)_3$, Br, NO_2

were prepared by the condensation of the corresponding phenols with thiocholesterine chlorocarbonate in absolute benzene in the presence of pyridine. They were purified by repeated recrystallization. Identity of the compounds was controlled by thin layer chromatography.

In the IR spectra of compounds so obtained intensive absorption bands are present at 1670–1730 cm^{-1} characteristic of the stretching vibrations of the carbonyl group, as well as the absorption band at 600–630 cm^{-1} characteristic of the stretching vibrations of the C—S group and the absorption band at 2820 cm^{-1} characteristic of the vibrations of the ether group C—O—C.

The mesomorphism of these compounds was studied by polarizing microscopy. The phase transition temperatures are summarized in Table 20. All the synthesized compounds possess cholesteric mesophase which is colourless on heating. Colour-temperature transitions are observed on cooling.

Introduction of substituents into the phenyl radical results in an increase of the phase transition temperatures with the increase of substituent bulkyness.

TABLE 20

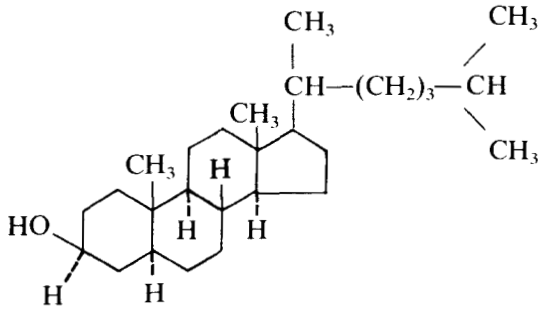
Mesomorphic properties of thiocholesterylarylcarbonates (XXIII)

		Temperature of phase transitions, °C	
No	X	T_{chol}	T_{is}
1	H	116.0	130.5
2	CH_3	122.0	129.0
3	C_8H_{17}	(99.5)	116.0
4	$C(CH_3)_3$	128.5	141.0
5	Br	122.0	130.0
6	NO_2	143.0	148.0

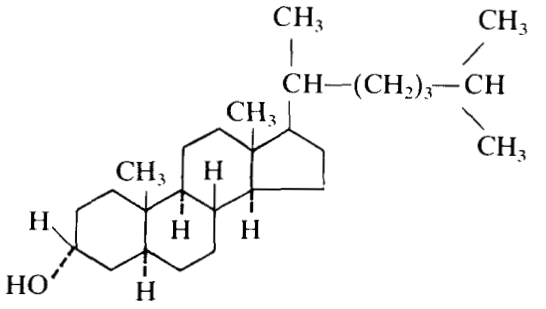
1.3. Cholesteric liquid crystals based on other steroids

The search for novel mesogens turned up derivatives of both cholesterine and other steroids.

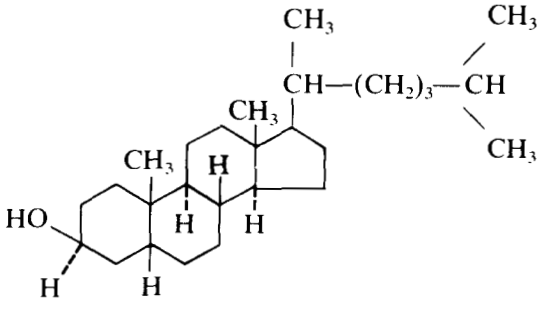
Wiegand[2,3] investigated the effect of substituents on the tendency to mesogeneity by the derivatives of cholestenol XXIV, epicholestanol XXV, coprostanol XXVI and epicoprostanol XXVII.



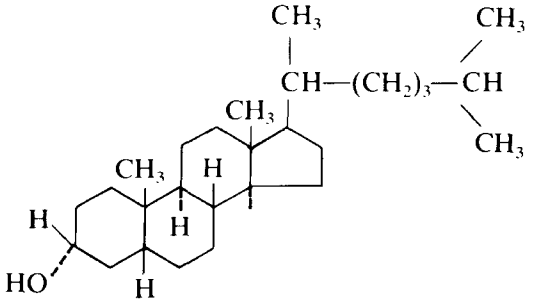
XXIV



XXV



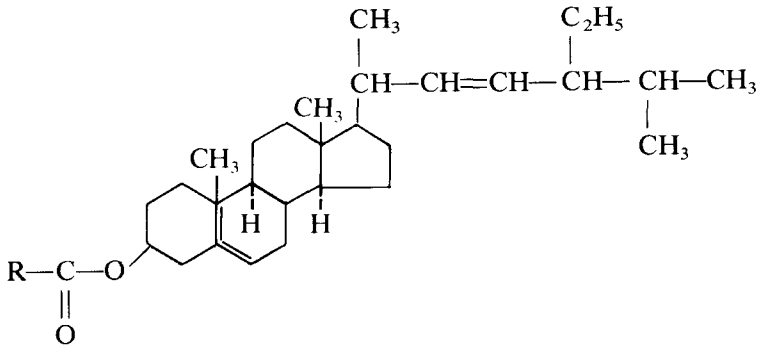
XXVI



XXVII

In Ref. 2 the effect of moving the double bonds in the cyclopentanperhydrophenanthrene fragment was studied. The position of the double bonds within the system of the rings of 3β-oxycholestenes and 3β-oxycholestedienes doesn't influence the transition temperature to the isotropic liquid, however, with the movement of the double bond into position C_{14-15} mesomorphism disappears. On the basis of experimental data Wiegand concluded that mesogeneity is characteristic of steroid derivatives with the rings in the trans-configuration containing substituents in the 3β-position.

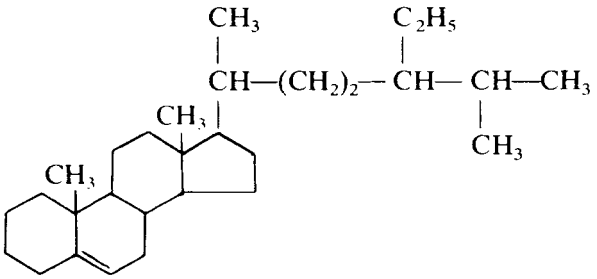
Esters of stigmasterine XXVIII possess only smectic mesomorphism.[75]



XXVII

$R = C_nH_{2n+1}$
$N = 1\text{–}11, 13, 15, 17$

This type of mesophase is characteristic of β-sitosterine ethers XXIX, their properties are described in Ref. 76.

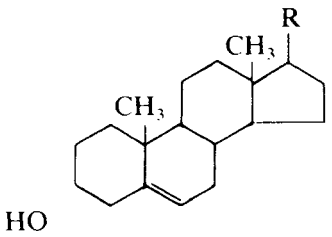


XXIX

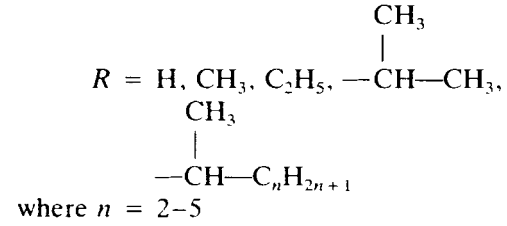
$R = C_nH_{2n+1}$
$N = 1-3, 5, 6, 8$

Introduction of an acyl radical containing the phenyl group into the 3β-position of compounds XXIX results in the appearance of the cholesteric mesophase.[77]

Pohlmann and Elser[78] considered the mesomorphism and structure of 17β-alkylsubstituted androstene (XXX). In this work it was shown that introduction of an oxy-group into the alkyl chain of steroids in the 17β-position causes an increase of the phase transition CLC → IL.



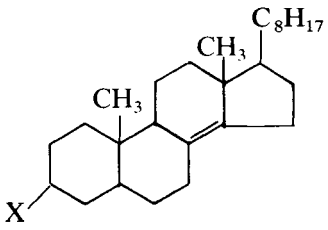
XXX



where $n = 2-5$

The results of a study of mesomorphism of different homologous series of steroids are given in Ref. 18.

Leder in his works[79,80] didn't alter the radical in the 17-β-position of the steroid system but varied the position of the double bond in the system of rings and the character of the radical in the 3β-position. We have synthesized different derivatives of doristerol XXXI.



XXXI

where X = Cl, —O—C(=O)—R, —O—C(=O)—O—R
R = alkyl

The synthesized compounds XXXI exist in the cholesteric mesophase at relatively low temperature (50–83°C).

All of the above indicates the variety of the current techniques for the preparation of CLC and underlines that the possibilities of the synthesis of novel compounds are really numerous in this domain.

2. STUDY OF THE PARAMETERS OF THE SUPRAMOLECULAR STRUCTURE OF CHOLESTERIC LIQUID CRYSTALS

The high sensitivity of the macroscopic properties of mesophases towards rather minor changes of molecular structure is due to the short-range forces of intermolecular interaction, in particular, induction and dispersion ones. The energies of these interactions are as follows:

$$E_{\text{ind}} = -\frac{2\alpha\mu^2}{r^6}; \qquad E_{\text{dis}} = -\frac{3\mathcal{I}\alpha^2}{4r^6}$$

where α—molecular polarizability, μ—dipole moment of the molecule, $\mathcal{I}$—ionization potential, r—effective distance between the centres of the molecular masses.

Since the values of the energies of induction and dispersion contribute considerably to the energy of intermolecular interaction at the formation of the mesophase and determine the values of its macroscopic parameters: temperatures of isotropic transitions—T_{is}, intervals of mesophase existence—ΔT, parameters of order—S, helical pitch—P, the connection of these parameters with the mesophase microcharacteristics: molecular structure, polarizability anisotropy—$\Delta\alpha$, average polarizability—$\bar{\alpha}$, dipole moment—μ, becomes apparent.

The present Chapter deals with investigations on the above classes—steroid derivatives—designed to find the connection between micro- and macrocharacteristics of the mesophase.

2.1. Methods for measuring the CLC parameters

2.1.1. Polarizing microscopy

Samples for measurements were prepared between glass surfaces as thin layers with their thickness determined by the gaskets. To obtain the cholesteric phase with confocal or plane texture the limiting conditions were assigned by different methods: special treatment of the glasses (polishing, introduction of surfactants), selection of the sample thickness, variation of the temperature regime of mesophase formation etc.

Identification of the mesophases and the determination of their temperature interval was carried out between the crossed polaroids of a microscope in a special thermostated cell which provided temperature stabilization up to 0.2° and different regimes of heating and cooling. It should be noted that the usual procedures for obtaining the plane texture in CLC are not always successful. Samples with confocal texture do not show bright colours of the selective reflection preventing the measurement of the temperature dependence of the helical pitch, $P(T)$. Therefore, we worked out the technique for measuring $P(T)$ as described below.

2.1.2. Method of selective reflection for the determination of the helical pitch

The helical pitch of CLC can be determined using the maxima of the selective reflection of light following the relation:

$$\eta_{max} = \bar{n}P, \qquad \bar{n} = \frac{1}{2}(n_0 + 2n_e) \tag{1}$$

where $\bar{n}$—mean index of CLC refraction depending weakly on the temperature, n_0—index of refraction of the ordinary ray, n_e—index of refraction of extra-ordinary ray.

To measure η_{max} the Scheme illustrated in Figure 3 was used. A light ray passing through monochromator 1 and reversing prism 2 in the microscope falls onto Sample 3. The size of the area illuminated on the sample is $\sim(0.01 \times 0.03)$ cm^2. After reflection from the sample and having passed through the microscope the light falls onto the ocular of microscope 4, where the magnified picture of the studied part of the sample is obtained. Registration of the maxima of the selectively reflected light from the confocal light texture was carried out using photoelectronic multiplier 5 and recording device 6.

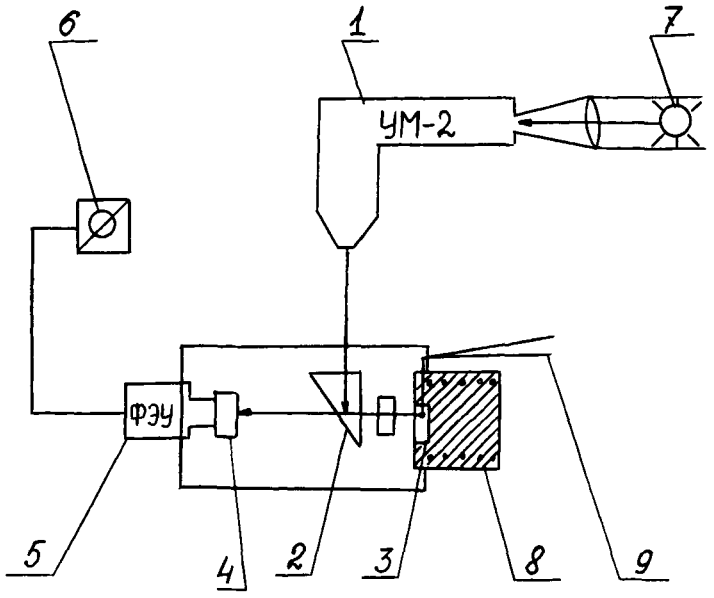


FIGURE 3 Schematic for determining the helical pitch by the method of selective reflection of light:

1—monochromator YM-2;
2—reversing prism;
3—the studied sample;
4—Microscope MBTY-42;
5—photomultiplier tube;
6—microammeter;
7—a light source;
8—thermal device;
9—thermocouple.

Stabilization of the temperature of the mentioned area of the sample ~0.1°, the error at the measuring of η_{max} was 1–2%.

2.1.3. *Refractometric method for the determination of the order parameter*

Determination of the temperature dependences of the order parameter $S(T)$ was accomplished based on refractometric measurements of $n_e(T)$ and $n_0(T)$ for CLC and the temperature dependences of the densities $\rho(T)$.[81] Values of n_e and n_0 were determined with an accuracy to 0.001° at η = 5893°; the temperature was thermostated to 0.1°. The accuracy of the density measurement ρ was 0.0002 g/cm^2; dependences $\rho(T)$ were treated with the method of least squares.

The measured values of n_e, n_0 and ρ, taking into account the anisotropy of the local field of CLC and its symmetry, were used for the calculation of the order parameter worked out in Ref. 81 as:

$$S = \frac{M}{4\pi N_A \rho \bar{f}} \cdot \frac{(n_e + n_0)\Delta n}{\Delta\alpha_0} \tag{2}$$

where M—molecular weight, N_A—Avogadro number, $\Delta\alpha_0$—anisotropy of molecular polarizability determined by extrapolation of the dependence corresponding to S = 1—the full ordering of CLC. The order parameter S depends on T as follows:

$$S = S_0(1 - T/T^*)^\eta , \tag{3}$$

where S_0 = 1 (or the more accurate expression is used $S_0 = \Delta\alpha_0/\alpha$),[82] T^*—temperature of overheating at the transition from the cholesteric phase to the isotropic one. The local average field for CLC is corrected according to Vuks' formula:

$$\bar{f} = \frac{\bar{n}^2 + 2}{3} \tag{4}$$

2.2. Temperature dependence of the helical pitch

The temperature dependences $P(T)$, presented partly in Ref. 83, were obtained using correlation (1) (See Figures 4a and 4b). As follows from those Figures, all the dependences $P(T)$ are, in general, linear except for those CLCs which form smectic mesophases (for example, cholesterine α-Cl-pelargonate). However, in some cases

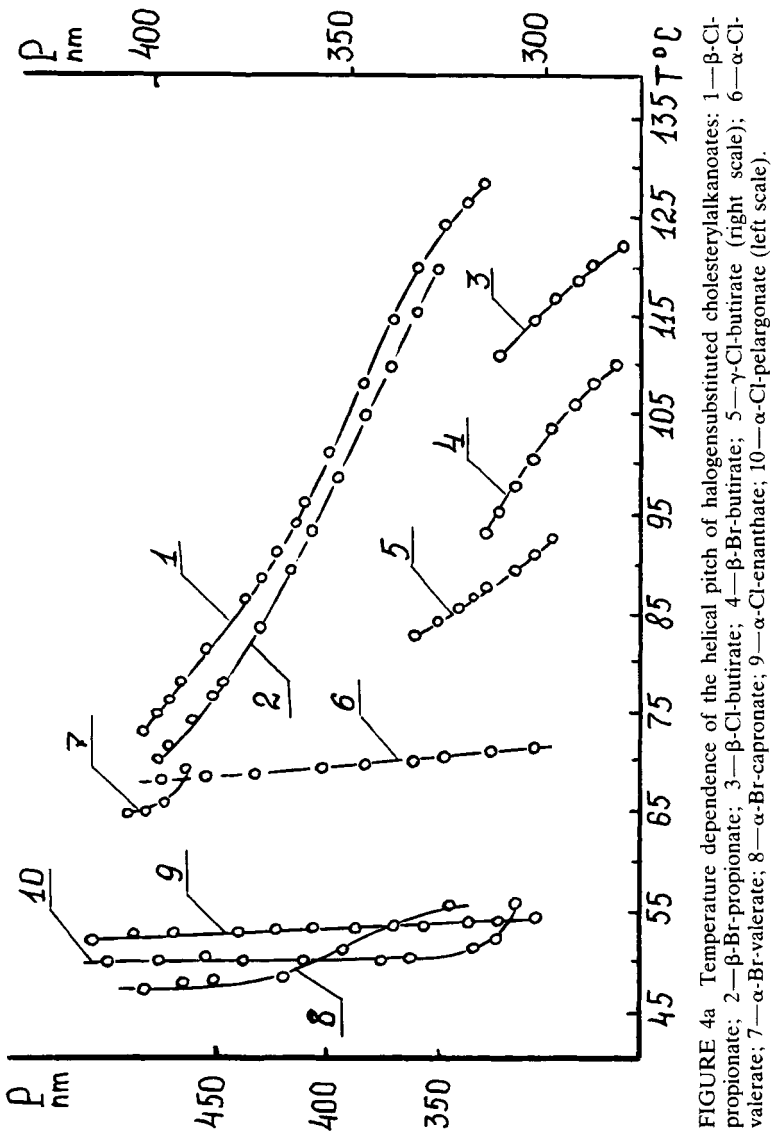


FIGURE 4a Temperature dependence of the helical pitch of halogensubstituted cholesterylalkanoates: 1—β-Cl-propionate; 2—β-Br-propionate; 3—β-Cl-butirate; 4—β-Br-butirate; 5—γ-Cl-butirate (right scale); 6—α-Cl-valerate; 7—α-Br-valerate; 8—α-Br-capronate; 9—α-Cl-enanthate; 10—α-Cl-pelargonate (left scale).

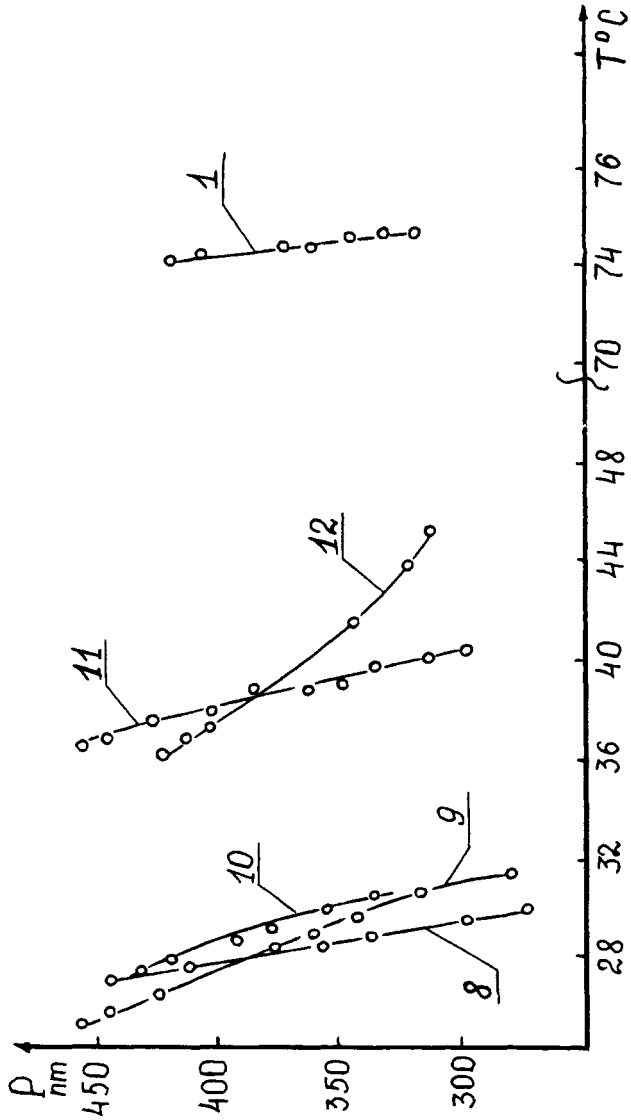


FIGURE 4b Temperature dependence of the helical pitch of halogensubstituted thiocholesterylalkanoates (numbering corresponds to the numbers of the compounds in Table 18).

non-linear parts are observed connected with pre-transition processes: at the transition into the isotropic state the dependence $P(T)$ falls sharply and near the crystallization point it increases. The slope of linear sections of the dependences $P(T)$ depends on the position of the halogen and the length of the alkyl chain. It increases considerably for α-halogensubstituted esters of cholesterine as well as with the lengthening of the alkyl chain. In the series of α-substituted cholesterine and thiocholesterine esters the slope of $P(T)$ is greater for the thioesters which corresponds to their higher thermosensitivity clearly seen when considering the dependences of the twisting angle θ on $T(\theta \sim 2\pi/n)$.

The character of the temperature dependence $P(T)$ in the studied class of compounds* is presented in Figure 5, since according to (1) η_{max} is proportional to P, and $\bar{n}$ does not depend significantly on the temperature. The dependences $\eta_{max}(T)$ are linear except for curve 3 where the decrease of η_{max} near $T_{is.}$ is due to the sharp decrease of the value of $S(T)$. Substantial disturbance of coplanarity of molecules (Z-isomers, halogensubstituted esters, thioesters) results in an increase of temperature sensitivity and a decrease of mesophase thermostability. Decrease of $T_{is.}$ is connected with the "loose" packing of the molecules in mesophase.

Data showing the behaviour of the helical pitch on the temperature for cholesterylcarbonates are given in Figure 6. The dependences are in general linear except in temperatural ranges corresponding to pretransition phenomena. Deviation from linearity is observed mostly with ortho-substituted phenylcholesterylcarbonates and is due to the sharp decrease of the order parameter near $T_{is.}$. Dependences $P(T)$ for para-substituted phenylcholesterylcarbonates indicate the high degree of ordering in the cholesteric phase.

Introduction of substituents into the benzene ring results in the increase of the anharmonicity U_v, parameter of molecular vibrations since atoms or atom groups protruding from the basic plane of the molecules represent an additional source of anharmonicity. As Figure 7 shows, the slope of the curve of the temperature dependence $\theta/T/T_{is}$ is determined by the parameter $U_v(\theta = \theta_0 + U_v(t/S(t)))$. Substituents in the ortho-position, which protrude from the basic plane of the molecules, increase the parameter U_v which results in the increase of the angle of the slope of $\theta/T/T_{is}$. Dependences $\theta/T/T_{is}$ for para-substituted phenylcholesterylcarbonates possess a smaller slope. Thus, ortho-substituted phenylcholesterylcarbonates are more thermosensitive cholesterics than para-substituted ones.

* Substituted cholesterine acrylates.

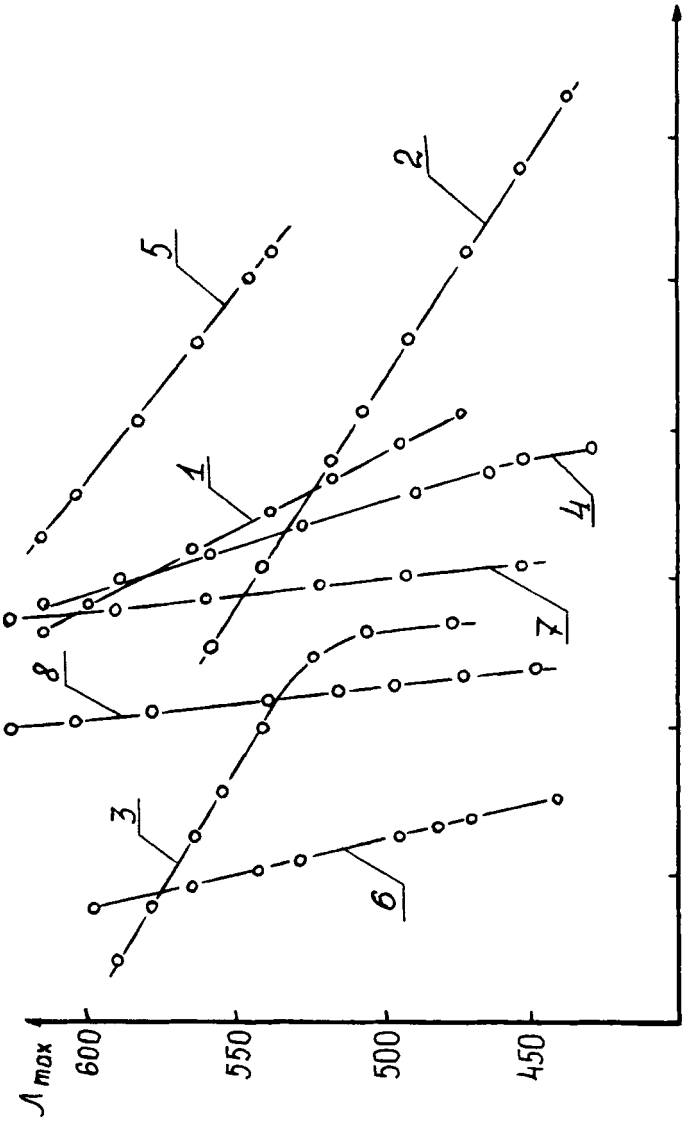


FIGURE 5 Temperature dependence of the helical pitch of substituted cholesterylacrylates: 1—cholesterylacrylate; 2—cholesterylcinnamate (trans); 3—cholesterylcinnamate (cis); 4—cholesterylchlorocinnamate (trans); 5—cholesterylcrotonate (trans); 6—cholesterylcrotonate (cis); 7—cholesterylchlorocrotonate (*Z*); 8—cholesterylchloroisocrotonate (*E*).

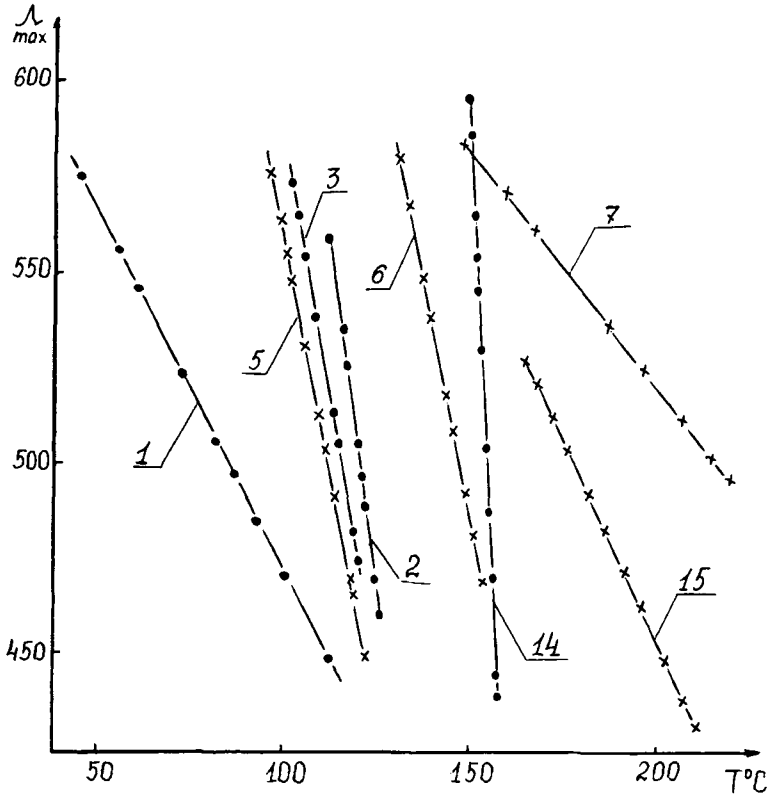


FIGURE 6 Temperature dependence of the helical pitch of substituted phenylcholesterylcarbonates (numbering of the straight lines corresponds to the numbers of the compounds in Table 13).

2.3 Temperature dependence of the order parameter

The most characteristic dependences of the order parameter on the temperature $S/T/T_{is}$ for the compounds under study are given in Figure 8. There is also the observed dependence of the S parameter value[84,90] on the type and position of halogens in the alkyl chain, on the length of this chain and on the substitution of an ester oxygen for sulphur. First of all, within the region of minor changes of S its values are higher for halogensubstituted cholesterine esters than for ordinary cholesterine esters.[85] At the transition from unsubstituted cholesterine esters to halogensubstituted ones Cl or Br atoms stabilize the alkyl chain as they are "heavier" than the H atom, thus increasing the ordering of the mesophase. Similarly, halogensubstituted choles-

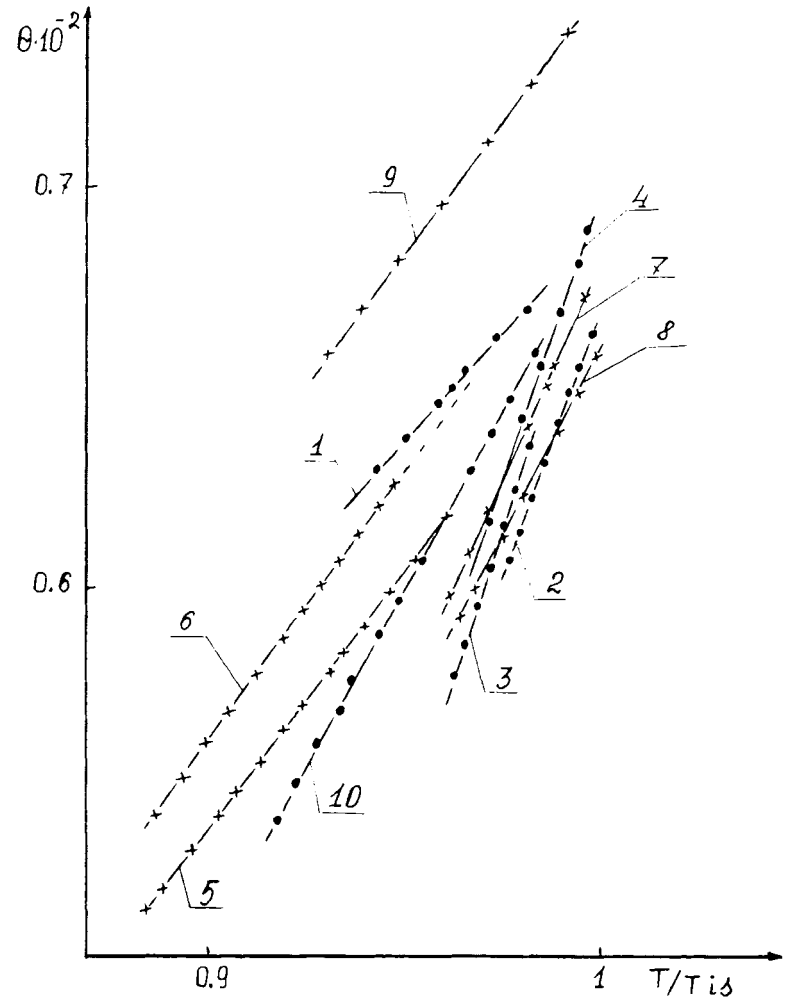


FIGURE 7 Dependence of the angle of helix twisting on thermal sensitivity for substituted cholesterylphenylcarbonates (numbering of the straight lines corresponds to the numbers of the compounds in Table 13).

terine esters possessing halogen, with a larger atomic weight as a substituent, reach greater S value (Cf. curves 1 and 2; 3 and 5).

It should be noted that the lengthening of the alkyl chain promotes the growth of S (curves 6, 7 in Figure 8), while halogen on the γ-position increases its mobility which is accompanied by a decrease of the S value (curve 4). Considerable decrease of S values is observed with thiocholesterine esters (curve 8). This is related to the fact that

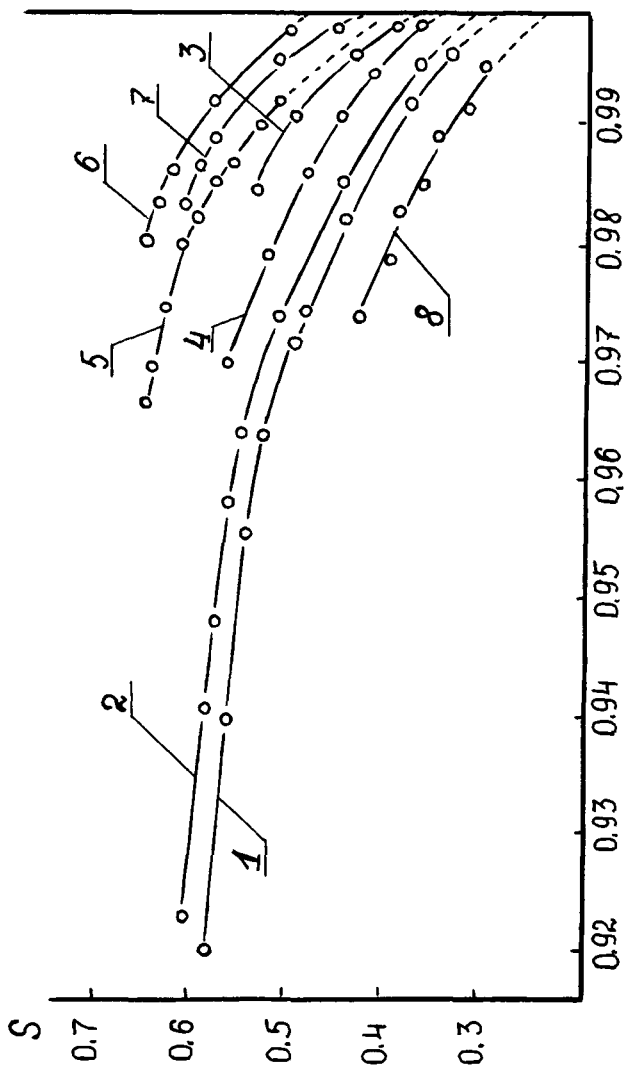


FIGURE 8 Temperature dependence of the order parameter of halogensubstituted cholesterylalkanoates: 1—β-Cl-propionate; 2—β-Br-propionate; 3—β-Cl-butirate; 4—γ-Cl-butirate; 5—β-Br-butirate; 6—α-Br-capronate; 7—α-Cl-pelargonate; 8—thiocholesterine α-Cl-pelargonate.

substitution of an ester oxygen for sulphur results in an increase of the acoplanarity of the molecular structure and it, in its turn, results in a less dense packing of the thiocholesterine molecules thereby affecting the S values.

2.4 Connection of molecular characteristics with macroscopic parameters

2.4.1. Effect of molecular anharmonicity on mesomorphism

The theory of helical twisting is based on the angular dependence of the energy of the intermolecular interaction of chiral molecules of the neighbouring quazinematic layers. Using a quantum mechanical theory of excitations Goossens has obtained the potential of interaction between two molecules $V(\theta)$ and an expression for the angle of helix twisting $\theta_0 = 2\pi/P_0$ which doesn't suggest any temperature dependence of θ_0.[86] This suggestion doesn't agree with the real behaviour of the cholesteric helix.

Another approach to the description of helix twisting is provided by the suggestion of Keating,[87] where the minimum of energy is achieved at $\theta_0 = 0$, but the potential $V(\theta)$ is asymmetric due to the chirality of the molecules. Averaging the twisting angle θ with time and taking into account that molecules make anharmonic twisting vibrations, Keating obtained an expression for the temperatural dependence $\theta(T)$ describing the behaviour of the helical pitch near the transition to the smectic phase. Both of the above approaches describe the limiting cases of the behaviour of $\theta(T)$ for CLC.

As it is shown in Ref. 88 the correctly chosen potential allows one to describe the dependence $P(T)$ for the most characteristic behaviour of the CLC helix. The expression for the twisting angle is as follows:

$$\theta_p = \theta_0 + U_v \frac{t}{S(t)} \tag{6}$$

where θ—the twisting angle according to Goossens, U_v—the parameter of anharmonicity of the rotational vibrations of the molecules, t—the variable T/T_{is}. The U_v value increases regularly with the introduction of substituents, serving as a potential source of anharmonicity of the rotational vibrations, into the mesogenic molecule. Since for halogensubstituted cholesterine and thiocholesterine alkanoates we had experimental data on the dependences $P(T)$ and $S(T)$ we were able to evaluate real values of θ_0 and U_v for a particular CLC. In Table 21 the values are given of θ_0 and U_v for some substi-

TABLE 21

Values of the torsion angle and anharmonicity parameter of the rotational vibrations of molecules of halogensubstituted cholesterine and thiocholesterine alkanoates

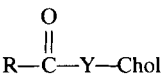
$$\bar{f} = \frac{\bar{n}^2 - 2}{3} - \frac{2[(n_e + n_0)\Delta n]^2}{27[\bar{n}^2 - 1 - (n_e + n_0)\Delta n/3]}$$

$$S = S_0(1 - T/T^*)^\eta$$

$$\bar{f} = \frac{\mu(\bar{n}^2 - 1)}{4\pi N_A \rho \bar{f}}$$

$$\theta_p = \theta_0 + U_v \frac{t}{S(t)}; \quad t = T/T_{is}$$

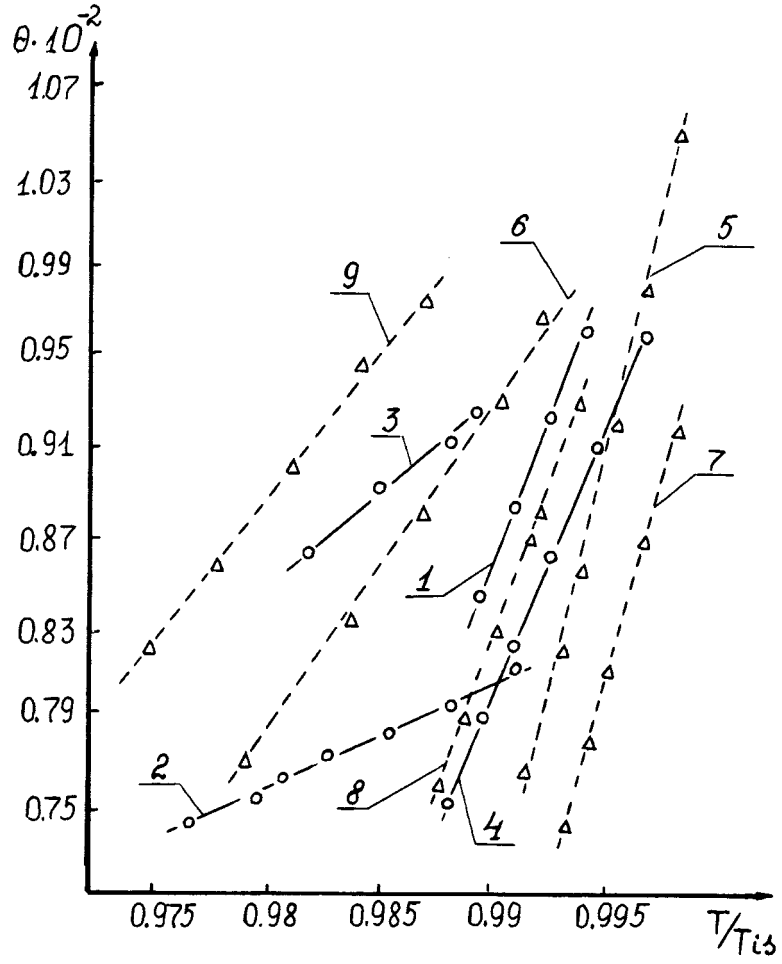
$$S = \frac{\mu(n_e + n_0)\Delta n}{2\pi N_A \rho f \Delta\gamma}$$



R	Y	$\theta_0 \cdot 10^{-2}$	$U_v \cdot 10^{-2}$
$CH_2(Cl)CH_2$—	O	0.81	0.07
$CH_2(Br)CH_2$—	O	0.80	0.05
$CH_3CH(Cl)CH_2$—	O	0.90	0.09
$CH_2(Cl)CH_2CH_2$	O	0.74	0.14
$CH_3CH_2CH(Br)$	O	0.91	0.10
$CH_3(CH_2)_6CH(Cl)$	S	0.76	0.50

tuted cholesterine and thiocholesterine alkanoates differing in the substituents nature and position in the α-position and in the terminal one. Lengthening of the alkyl chain increases considerably θ_0 but influences U_v less. All the substituents which protrude the most from the basic molecular plane cause an increase of the U_v parameter, for example, in the case of thiocholesterine α-Cl-pelargonate (Table 21). The question of the connection of the anharmonicity parameter with the structure of the molecules of the substituted cholesterine alkanoates is dealt with in detail in Refs. 89 and 91.

The U_v parameter due to the molecular structure determines directly the macroscopic properties of the mesophase. With the increase of U_v the mesophase interval decreases, i.e., the thermostability of the CLC increases. This is mostly seen with the dependence $\theta/T/T_{is}$ within the region of small changes of S and linear dependences of $P(T)$ (Figures 9 and 10). For α-halogensubstituted cholesterine alkanoates the halogen atom causes a decrease of the amplitude of



R—C—O—Chol
||
O

R = 1—$CH_3(CH_2)_2CH(Cl)$—
2—$CH_3(CH_2)_2CH(Br)$—
3—$CH_3(CH_2)_3CH(Br)$—
4—$CH_3(CH_2)_4CH(Cl)$—

R_1—C—S—Chol
||
O

R_1 = 5—$CH_3(CH_2)_2CH(Cl)$—
6—$CH_3(CH_2)_2CH(Br)$—
7—$CH_3(CH_2)_3CH(Br)$—
8—$CH_3(CH_2)_4CH(Cl)$—
9—$CH_3(CH_2)_6CH(Cl)$—

FIGURE 9 Dependence of helix twisting angle on thermal sensitivity of cholesterine and thiocholesterine.

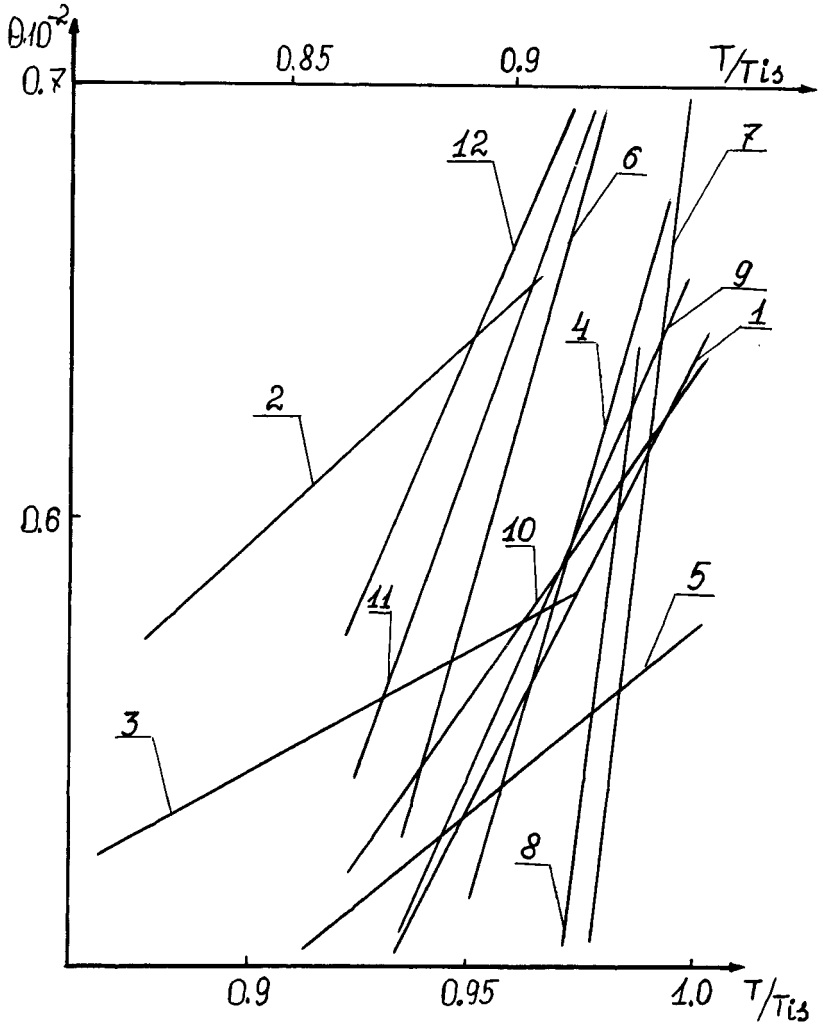


FIGURE 10 Dependence of helix twisting angle on thermal sensitivity of substituted cholesterine acrylates. Upper scale corresponds to the straight line *N* 2 (numbering of the straight lines corresponds to the numbers of the compounds in Table 9).

the twisting vibrations of the alkyl chain which cause the anharmonicity of the vibrations (Figure 9). Thus, the slope $\theta/T/T_{is.}$ is noticeably reduced with the substitution of Cl for Br (Cf. curves 1 and 2; 3 and 4). For α-halogensubstituted thiocholesterine alkanoates the slope $\theta/T/T_{is.}$ increases since sulphur represents an additional source of anharmonicity; this source is so powerful that at the transition from

α-bromosubstituted thiocholesterine alkanoates to α-chlorosubstituted thiocholesterine alkanoates the slope $\theta/T/T_{is}$ does not change considerably (Cf. curves 5 and 6; 7 and 8).

The value of the vibrational anharmonicity for the derivatives of unsaturated carboxylic acids and cholesterine depends on molecular isomerism. *E*-isomers possess smaller U_v values as compared with their *Z*-isomers (Cf. curves 2 and 3; 5 and 6 in Figure 10). In this series of compounds a considerable effect is observed of the halogen atoms on the slope $\theta/T/T_{is}$ (Cf. curves 4 and 3), while the contribution of the sulphur atom in the transition from cholesterine derivatives to thiocholesterines is not large (Cf. curves 10 and 2; 9 and 1; 10 and 4). Thus, thermosensitivity of CLC being a macroscopic characteristic is determined by the microscopic parameter U_v which is directly connected with the molecular structure. Introduction of substituents, transition to *Z*-isomers, the presence of molecular fragments protruding over the basic plane represent an additional source for the anharmonicity decreasing ΔT.

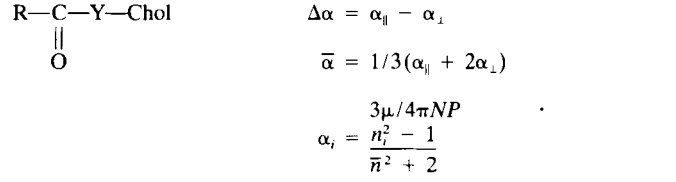
2.4.2. *Dependence of mesomorphic properties on molecular polarizability and dipole moment*

Analysis of the electronic structure of the molecules of cholesterine and thiocholesterine alkanoates shows that the dipole moment μ of the molecules is determined mainly by the electron density localized on the carbonyl group and changes not considerably within the homologous series. Consequently, the mesomorphic properties of this class of compounds are mainly determined by their molecular polarizability.

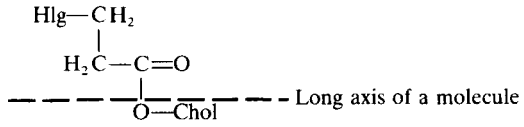
We have used two approaches to determine the molecular polarizability within the studied series of substituted cholesterine and thiocholesterine alkanoates: an additive scheme and experimental determination based on refractometric and densitometric measurements. The additive scheme suggests that the presence of three main directions in a molecule corresponding to α_1, α_2 and α_3 are the main values of the molecular polarizability tensor. For molecules of cholesterine alkanoates possessing no axial symmetry we can't find these directions and propose to consider the long axis of the molecule (corresponding to $\alpha_{\parallel}$) and the two axes perpendicular to it (corresponding to $\alpha_{\perp}$) as the axes of symmetry. For cholesteric molecules it is suggested that $\bar{\alpha} = -1/3(\alpha_{\parallel} + 2\alpha_{\perp})$ is the mean value of the polarizability and $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$—the polarizability anisotropy. In Table 22 their numeric values are given calculated using an additive scheme. An increase of the polarizability anisotropy is observed due

TABLE 22

Molecular polarizabilities of halogensubstituted alkanoates



R	Y	T_{is}, °C	Additive ᾱ, Å³	Additive Δα, Å³	Experiment ᾱ, Å³	Experiment Δα, Å³
CH_3CH_2—	O	111.8	59.73	34.34	52.62	4.59
CH_2ClCH_2—	O	129	61.82	35.14	55.06	6.50
CH_2BrCH_2—	O	120	62.89	35.28	57.35	6.51
$CH_3(CH_2)_2$—	O	113	61.74	34.70	51.55	4.52
$CH_3CHClCH_2$—	O	123	63.98	35.57	57.21	4.41
$CH_3CHBrCH_2$—	O	110	65.07	35.74	57.86	5.26
$CH_3Cl(CH_2)_2$—	O	89	63.83	35.49	56.28	4.90
$CH_3(CH_2)_4$—	O	101.5	65.75	35.40	58.72	3.98
$CH_3(CH_2)_3CHBr$—	O	55	69.08	36.45	63.01	4.80
$CH_3(CH_2)_4$—	S	107.7	69.17	35.93		
$CH_3(CH_2)_3CHBr$—	S	65	72.53	37.06	64.95	5.04
$CH_3(CH_2)_7$—	O	92	71.76	36.48	63.15	5.89
$CH_3(CH_2)_6CHCl$—	O	64.4	74.00	37.34	66.38	4.89
$CH_3(CH_2)_6CHCl$—	S	51	77.46	37.95	68.37	2.42



to the introduction of a halogen atom into the alkyl chain and the substitution of an oxygen atom for a sulphur one in the ester group. Evidently, the values given in Table 22 relate to the case of non-interacting molecules and can give only indirect information about the role of molecular polarizability in mesophase formation. For a further analysis of $\alpha_{\parallel}$ and $\alpha_{\perp}$ we have used the Lorentz-Lorenz formula

$$\alpha_i = \frac{3M}{4\pi N_A \rho} \cdot \frac{n_i^2 - 1}{\bar{n}^2 + 2} \tag{7}$$

where M—molecular mass, N_A—Avogadro number, ρ—density of the substance, n_i—indices of the refraction of the quasinematic layer of CLC. The local field is taken into account as in (4). The connection of the indices of CLC refraction (n_0 and n_e) determined by refrac-

tometry at $\eta = 5893$ Å with the indices of refraction of the quasi-nematic layer ($n_\parallel$ is parallel to the long axis of the molecule, $n_\perp$ is perpendicular to the long axis of molecule) is given as follows:

$$\begin{cases} n_\parallel^2 = 2n_0^2 - n_e^2 \\ n_\perp^2 = n_e^2 \end{cases} \tag{8}$$

In Table 22 the values of $\alpha_\parallel$, $\alpha_\perp$, $\Delta\alpha$ and $\bar{\alpha}$ are given as calculated at temperatures close to crystallization. Comparison of these values with those obtained according to the additive scheme indicates that at mesophase formation $\alpha_\parallel$ value decreases, while $\alpha_\perp$ increases in such a way that the $\bar{\alpha}$ value for non-interacting molecules and in mesophase doesn't change significantly, but the polarizability anisotropy increases by almost an order of magnitude. The molecule in CLC is "twisting" somewhat in order to achieve the minimum of the energy of intermolecular interaction. Molecular "twisting" probably provides the anisotropy of the forces of intermolecular interaction which results in the appearance of the cholesteric helix.[92]

Analysis of the results of Table 22 shows that the T_{is} value increases with the increase of $\Delta\alpha$ and decreases with the increase of $\bar{\alpha}$ which allows one to state the essential role of dispersion interaction within the class of halogensubstituted cholesterine alkanoates at mesophase formation. Introduction of substituents, lengthening of the alkyl chain result in steric effects preventing the approach of the molecules. This causes the decrease of the energy of dispersion interaction as well as the reduction of T_{is}.

In the class of the derivatives of unsaturated carboxylic acids and cholesterine, and their thioanalogues, the conjugation effects determine the degree of the contribution of the induction energy (E_{ind}) to the full energy of intermolecular interaction. Since E_{ind} is determined by the μ value T_{is} must also depend on μ. Values of the dipole moments of model molecules were obtained by calculation according to the CNDO/2 method. For halogensubstituted esters and their thioanalogues the calculation of the dipole moments took into account the vacant α-orbitals. The values of the dipole moments of the *E*-isomers are greater than those of the *Z*-isomers (Table 10) due to the effects of π-conjugation. Introduction of donor groups (methyl-, phenyl-) also promotes the increase of μ. The transition from esters to thioesters is accompanied by a decrease of the dipole moment since the valence angle C—O—C is larger than C—S—C. In Figure 2 the T_{is}/μ dependence is presented allowing one to draw the conclusion

that the considerable contribution of the induction energy to the full energy of intermolecular interaction is responsible for mesophase formation. Thus, in the class of the derivatives of esters of unsaturated carboxylic acids and cholesterine the induction interaction energy is of special importance. Estimation of the relation $E_{dis}/E_{ind} = 3/8\Im\bar{\alpha}/\mu^2$ for the two classes of compounds indicates that $E_{dis}/E_{ind} \sim 18 \div 20$ in the case of halogensubstituted cholesterine alkanoates, while for the derivatives of esters of unsaturated carboxylic acids and cholesterine this value changes within the range 20–2, i.e., for the esters with the greater dipole moment the value of the dispersion energy is comparable with that of the induction energy.

Thus, the analysis of the physico-chemical characteristics of mesophase in the class of halogensubstituted cholesterine and thiocholesterine alkanoates and the esters of substituted unsaturated acids of cholesterine and thiocholesterine has shown that forces of induction and dispersion interactions are of determining importance for mesophase formation.

The largest contribution of dispersion interactions is observed in the series of halogensubstituted cholesterine and thiocholesterine alkanoates with the macroscopic characteristics depending on the molecular polarizability.

Induction interaction contributes greatly to the energy of mesophase formation within the series of the derivatives of esters and thioesters of unsaturated carboxylic acids and cholesterine showing itself in the dependence of mesophase thermostability, the interval of its existence, on the value of the dipole moment.

CONCLUSIONS

The study of the effect of the molecular structure of liquid crystals (including cholesteric) on their mesogenic ability and mesomorphic properties has received a great deal of attention.

Up to now a large number of liquid crystals of cholesteric type were synthesized based on various steroids. Considerable experimental material is available on the determination of their mesomorphic characteristics (mesophase range, thermostability, etc). Supramolecular structure is being successfully investigated, its characteristics such as helical pitch and order parameter are determined as well as their temperature dependences. Attempts are being made to estimate quantitatively the effect of fine chemical structure on the parameters of the supramolecular structure.

The series of cholesterine and thiocholesterine derivatives (halogensubstituted alkanoates, unsaturated acids esters, carbonates) reveals the effect of the dipole moment and molecular polarizability, which are responsible for some forces of intermolecular intersection, on the compounds mesomorphic properties.

It was found that within the series of halogensubstituted cholesteryl- and thiocholesterylalkanoates the forces of dispersion interaction, depending mainly on the compounds molecular polarizability, are of determining importance for mesophase formation.

The forces of induction interaction, depending considerably on the dipole moments of the molecules, also influence mesophase formation within the series of the esters of cholesterine as well as thiocholesterine and unsaturated carboxylic acids.

The generally accepted theory proposed by Goossens for the formation of cholesteric liquid crystals fails to explain a number of experimental observations, for example, the temperature dependence of cholesteric helical pitch. The theory of Goossens predicts a slight increase of the pitch near the temperature of isotropic transition, while in practice a considerable increase of the pitch is observed with a decrease of the temperature. The theory of Keating is in partial agreement with this statement.

Considering the molecules of cholesteric liquid crystals as anharmonic oscillators and using Keating's equation, including the parameter of the anharmonicity of the twisting vibrations of the molecules, it was shown that some mesomorphic properties of the compounds, for example, thermostability, are determined by this parameter. Thus, it could be concluded that the introduction of certain substituents affecting the anharmonicity of the molecular vibrations results in a change of the mesomorphic properties of the compounds.

To summarize, it should be noted that the question of the connection of the structure of steroid derivatives with their mesomorphic properties is still left open, in spite of the positive results obtained.

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