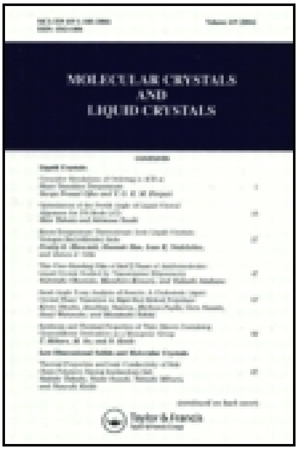

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Mesomorphogens: IV

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Version of record first published: 14 Oct 2011.

To cite this article: A. V. Bogatsky, A. I. Galatina & N. S. Novikova (1981): Mesomorphogens: IV, Molecular Crystals and Liquid Crystals, 66:1, 241-246

To link to this article: http://dx.doi.org/10.1080/00268948108072677

Mol. Cryst. Liq. Cryst., 1981, Vol. 66, pp. 241–246
0026–8941/81/6604–0241 $06.50/0

Printed in the U.S.A.

Mesomorphogens: IV

Liquid-Crystal Compounds Based on Thiocholesterol

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(*Received July 28, 1980*)

In recent years, heighted interest has been shown in thiocholesterol and its derivatives. First of all, some thiocholesterol esters derived from ω-phenylalkanoic acids possess highly temperature-sensitive thermotropic cholesteric liquid crystal phases.[1] At present however, there are not sufficient data about the mesomorphism of thiocholesterol derivatives, for apart from the above esters, only unsubstituted *n*-alkanoates[2] and *n*-alkyl carbonates[3] of thiocholesterol have been studied and described.

Substitution of the oxygen atom in the cholesterol molecule by the more bulky and less electronegative sulphur atom leads to considerable changes in the mesomorphic characteristics of the derivatives. Tishenko and Cherkashina[4] have described the effects in detail.

As a result of our investigations, the influence of a halogen atom upon the mesogenic qualities of cholesteryl alkanoates was established.[5] Thus, the introduction of the electronegative halogen into the α-position of the ester group of cholesteryl alkanoates, when the number of carbon atoms, $n < 5$, leads to the loss of mesogenic properties. On increasing the alkyl chain length ($n \geqslant 5$), the mesogenic properties are restored. When the halogen atom is in the β- or -γ- position, the mesophases are of wide temperature range and exhibit bright colours. It should be noted at this point that there is no dependence of the liquid-crystal properties on the length of the alkyl substituent. These facts can be explained by the influence of polar and steric factors.

Taking into account the above distinctions between cholesteryl and thiocholesteryl systems, it was of interest to study the influence of introducing a halogen atom into the alkyl chain of thiocholesteryl alkanoates and to compare the mesomorphic properties with those of the corresponding cholesteryl α-halogenoalkanoates.

Paper presented at the Eighth International Liquid Crystal Conference, Kyoto, Japan, June 30–July 4, 1980.

Usually thiocholesteryl esters are obtained by means of transesterification[6] and transacylation of the imidazolide;[7] the yields are high as compared with ordinary esterification by acids[8] or the acid chlorides of a number of acids.[9]

However, in spite of the high yields and purity of the thiocholesteryl esters, transesterification has been used mainly for higher fatty acids.

It was recognized that transacylation of the imidazolide using N,N'-carbonyldiimidazole was the most effective method of obtaining thiocholesteryl alkanoates. In this manner, unsubstituted thiocholesteryl alkanoates were obtained.[2] However, we succeeded in obtaining the thiocholesteryl esters of the halogeno-substituted acids by condensation of the acid chloride of the corresponding acid with thiocholesterol in a non-polar solvent, under an inert atmosphere, and in the presence of triethylamine, in satisfactory yield. The data on the yields and properties of the esters obtained are included in Table I. The compositions of the compounds were confirmed by elemental analysis; their structures were confirmed by IR-spectroscopy. The bands for the carbonyl group in the thioesters are at 1660–1690 cm^{-1}. The bands associated with C—S—C are observed within the 770–870 cm^{-1} range.

To check on purity of the above mentioned compounds, thin-layer chromatography on "Silufol-254" plates was used. A hexane: benzene (15:85) mixture was used as eluent.

IR spectra were recorded for the samples as KBr pellets using a "UR-20" spectrometer. Thiocholesterol was obtained and purified by well-known methods.[10–11] Acid chlorides of the halogeno-substituted acids were obtained by interaction of the acids and a surplus of thionyl chloride.

Temperatures of phase transitions were determined by means of the "MIN-8" polarizing microscope fitted with a heating stage. Dipole moments were measured using a "Tangens" dielcometer.

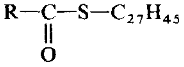
Our study of the halogeno-substituted thiocholesteryl alkanoates showed that in the case of slow cooling of the sample (approximately 2°C per minute), isotropic liquid-solid crystal transitions (crystallization) were observed. The cholesteric mesophase appeared only at high rates of cooling down to 0°C or to room temperature. Compounds I–III and VII–VIII give glasses keeping the cholesteric properties; the rest of the compounds possess a high viscosity in the liquid-crystal state. They do not crystallize even over a long period of time.

Because of the quick cooling required, it was impossible to determine the isotropic liquid-mesophase transition temperatures for most of the compounds. The cholesteric mesophase for the α-Cl-pelargonate of thiocholesterol existed for only a narrow temperature interval. In addition, the above compounds possess smectic mesophases.

All the comparative data on the mesomorphism of the α-halogeno-substituted cholesteryl esters and their thio-analogues are presented in Table II.

TABLE I

Substituted thiocholesteryl alkanoates



$R{-}C(=O){-}S{-}C_{27}H_{45}$

SL Nos	R	Rf Value (t.l.c.)	Yield (%)	Phase transition (°C) T_S	T_{Ch}	T_I	Crystallize on slow cooling (°C)	Found (%) Hal	S	Molecular formula	Required (%) Hal	S
I	$CH_3CH(Cl)$		71	—	—	90		6.93	6.02	$C_{30}H_{49}ClOS$	7.19	6.48
II	$CH_3CH(Br)$	0.43	67	—	—	92	61	14.33	5.73	$C_{30}H_{49}BrOS$	14.89	5.95
III	$CH_3CH_2CH(Cl)$	0.42	53	—	—	87	52.4	6.25	5.75	$C_{31}H_{51}ClOS$	7.00	6.31
IV	$CH_3CH_2CH(Br)$	0.42	54	—	—	79.6	78	14.50	5.81	$C_{31}H_{51}BrOS$	14.50	5.80
V	$CH_2(Cl)CH_2CH_2$	0.34	69	—	—	95		7.07	6.39	$C_{31}H_{51}ClOS$	7.00	6.31
VI	$CH_3CH_2CH(OC_6H_5)$		50	—	—	105			5.47	$C_{37}H_{56}O_2S$		5.66
VII	$(CH_3)_2CHCH(Cl)$	0.49	63	—	—	105.6	90.4	6.88	6.31	$C_{32}H_{53}ClOS$	6.82	6.14
VIII	$(CH_3)_2CHCH(Br)$	0.49	60	—	—	121	92.6	14.10	5.33	$C_{32}H_{53}BrOS$	14.15	5.56
IX	$CH_3(CH_2)_2CG(Cl)$	0.39	48	—	—	95	39.5	6.37	5.84	$C_{32}H_{53}ClOS$	6.82	6.14
X	$CH_3(CH_2)_2CH(Br)$	0.43	43	—	—	77.4	49.4	13.90	5.39	$C_{32}H_{53}BrOS$	14.15	5.56
XI	$CH_3(CH_2)CH(CH_3)$	0.36	60	(50)	—	82	47		5.90	$C_{33}H_{56}OS$		6.30
XII	$CH_3(CH_2)_4CH(Cl)$	0.30	40			88	57.7	6.10	5.50	$C_{34}H_{57}ClOS$	6.47	5.80
XIII	$CH_3(CH_2)_6CH(Cl)$	0.53	62	(41.6)	(43.4)	51		5.97	5.39	$C_{36}H_6{}^1ClOS$	6.15	5.55

Remarks: Compounds I–V, VII–X, XII, XIII show mesomorphic properties, while compounds I–III and VII, VIII become glassy. Compound VI does not show a mesophase.

TABLE II

Mesomorphic properties of α-halogeno-substituted cholestryl alkanoates and thiocholesteryl alkanoates

Nos	Thiocholesteryl esters	M.p. (°C)	Mesophase	Nos	Cholesteryl esters	M.p. (°C)	Mesophase
I	α-Cl-propionate	90	monotropic cholesteric on swift cooling	XI	α-Cl-propionate	121–3	none
II	α-Br-propionate	92	monotropic cholesteric on swift cooling	XII	α-Br-propionate	127–8	none
III	α-Cl-butyrate	87	monotropic cholesteric on swift cooling	XIII	α-Cl-butyrate	114–5	none
IV	α-Br-butyrate	79.6	monotropic cholesteric on swift cooling	XIV	α-Br-butyrate	118	none
V	α-Cl-*i*-pentanoate	105.6	monotropic cholesteric on swift cooling	XV	α-Cl-*i*-pentanoate	138	none
VI	α-Br-*i*-pantanoate	121	monotropic cholesteric on swift cooling	XVI	α-Br-*i*-pentanoate	142	none
VII	α-Cl-pentanoate	95	monotropic cholesteric on swift cooling	XVII	α-Cl-pentanoate	85	monotropic cholesteric
VIII	α-Br-pentanoate	77.4	monotropic cholesteric on swift cooling	XVIII	α-Br-pentanoate	78	monotropic cholesteric
IX	α-Cl-heptanoate	88	monotropic cholesteric on swift cooling	XIX	α-Cl-heptanoate	100.4	monotropic cholestic on swift cooling, selective reflection
X	α-Cl-nonanoate	51	monotropic cholesteric (43.6–41.6°C) and monotropic smectic	XX	α-Cl-nonanoate	64.4	monotropic cholesteric (55.6–51°C) and monotropic smectic

Essential distinctions between the mesomorphic properties are as follows:

a) α-halogeno-substituted cholesteryl alkanoates (compounds XI–XVI) have no mesogenic properties, but the thio-esters possess monotropic cholesteric mesophases;

b) the melting temperature of the α-halogeno-substituted thiocholesteryl esters is significantly lower than the melting temperatures of the analogous cholesteryl esters;

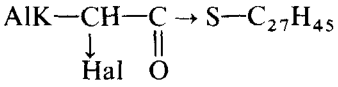
c) the α-halogeno-pentanoates of cholesterol (XVII–XVIII) show mesomorphic properties under conditions of rapid cooling;

d) smectic mesophases are observed for the present homologous series only when the alkyl chain contains no less than 9 atoms of carbon;

e) bright colours of selective reflection are observed for the cholesteric mesophases of the higher homologues of the α-halogeno-substituted cholesteryl alkanoates; this doesn't occur in the series of their thio-analogues.

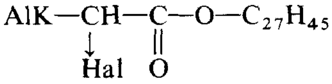
According to the experimental results, one must suppose that the volume and electronic character of the constituent atoms, namely the substituent in the α-position and the sulphur, exert a considerable influence upon the mesogenic qualities of the α-halogeno-substituted thiocholesteryl alkanoates. The bulky halogeno-substituent (in the case of the α-halogeno-substituted cholesteryl alkanoates (with the number of carbon atoms in the alkyl chain < 5) reduces the geometrical anisotropy of the molecules and causes the disappearance of the mesogenic properties. However, monotropic cholesteric mesophases are observed for the analogous thio-esters in spite of the halogen in the α-position.

Taking into consideration that the electronegativity of oxygen is significantly more than that of sulphur, the inductive effect in the case of



$$\mathrm{AlK{-}\underset{\underset{Hal}{\downarrow}}{CH}{-}\underset{\underset{O}{\|}}{C}\rightarrow S{-}C_{27}H_{45}}$$

will be less than that for



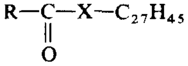
$$\mathrm{AlK{-}\underset{\underset{Hal}{\downarrow}}{CH}{-}\underset{\underset{O}{\|}}{C}{-}O{-}C_{27}H_{45}}$$

Therefore, interactions involving the carbonyl group will decrease, i.e., greater lateral attractions between molecules of the thiocholesteryl esters of the α-halogeno-substituted acids are assumed.

The values of the dipole moments presented in Table III decrease in the order α-halogeno-substituted cholesteryl alkanoates > α-halogeno-substituted thiocholesteryl alkanoates > unsubstituted cholesteryl alkanoates.

TABLE III

Dipole moments



$$R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}X{-}C_{27}H_{45}$$

R	X	μ_D
$CH_3CH_2CH_2$—	O	1.89
$CH_3CH_2CH(Br)$—	O	2.5
$CH_3CH(Br)CH_2$—	O	2.16
$CH_3CH_2CH(Br)$—	S	2.35
$CH_3CH_2CH(Cl)$—	O	2.59
$CH_3CH(Cl)CH_2$—	O	2.56
$CH_2(Cl)CH_2CH_2$—	O	2.37
$CH_3(CH_2)_6CH(Cl)$—	O	2.58
$CH_3(CH_2)CH(Cl)$—	S	2.23

On increasing the alkyl chain length, the geometrical anisotropy of the molecules is restored and the distinction between the mesomorphic properties of the present homologous series disappears.

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