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Mesomorphic Behaviour of Cholesteryl Esters
II: Trans-*p*-*n*-Alkoxy Cinnamates of Cholesterol†

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Abstract—A homologous series of cholesteryl (trans-*p*-*n*-alkoxy) cinnamates has been prepared by reacting trans-*p*-*n*-alkoxy cinnamoyl chlorides with cholesterol, and its mesomorphic behaviour studied. All the members of the series are enantiotropic mesomorphic. The lower members of the series exhibit cholesteric mesophases, whereas the higher members, starting with the decyloxy ester, are polymesomorphic, smectic and cholesteric. The smectic mesophase increases with an increase in the alkyl chain length at the cost of the cholesteric mesophase. The decyloxy and dodecyloxy esters also exhibit enantiotropic polymesomorphism of the smectic phase. The cholesteric mesophase persists up to the last member of the series. All the members of the series exhibit iridescent colours with a change in temperature; even the last member of the series exhibits this phenomenon which is not the case in the corresponding *n*-alkanoates or the *p*-*n*-alkoxybenzoates of cholesterol. At the juncture of the smectic-cholesteric transition a colour spectrum is observed both while heating as well as cooling. The thermal stabilities of the mesophases of the series are compared with those of the *n*-alkanoates and the *p*-*n*-alkoxybenzoates of cholesterol.

Introduction

The cholesteric mesophase exhibits some properties markedly different from smectic and nematic mesophases. Friedel(1) is of the opinion that the cholesteric phase is nematic in type. He based his conclusions from his study of cholesteryl compounds and the mixtures of cholesterol and nematogenic compounds. Gray(2) observes that when an isotropic liquid is cooled, the cholesteric mesophase

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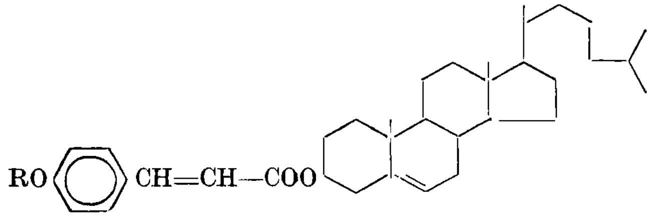
separates as bâtonnets like a smectic phase and coalesces to form focal-conic groups arising from layer structures in the mesophase. He argues that no direct smectic-isotropic transition, i.e. exhibition of a pure smectic phase is observed in cholesteryl compounds. Some cholesteric compounds(3) are, however, reported to exhibit pure smectic mesophases. Cholesteric compounds have fluidity like a nematic mesophase. They can be oriented by magnetic and electric fields like nematic mesophases.(4) These properties are indicative of the cholesteric mesophase to be of the highly ordered nematic mesophase. When two cholesteryl compounds with opposite optical rotatory power are mixed in different proportions, a stage comes when that mixture exhibits a nematic mesophase.(5) Recently it has been reported that racemic nematic compounds on double decomposition(6a) or by resolution exhibit a cholesteric mesophase.(6b–6c) As far as reported, all cholesteric compounds are optically active. It seems that, comparatively much less is known about the effect of chemical constitution on the mesomorphic properties of cholesteryl compounds, which may help in arriving at the similarity of the cholesteric mesophase to nematic or smectic mesophase, whereas the effect of the structure on nematic and smectic mesophases has been studied in detail. The present series was synthesized with a view that it may throw some light on chemical constitution and cholesteric liquid crystalline properties.

Results and Discussion

Fourteen esters of cholesterol have been synthesized by reacting different trans-*p*-*n*-alkoxycinnamoyl chlorides with cholesterol. The melting points and transition temperatures are summarized in Table 1. All the esters studied here exhibit enantiotropic mesophases. The transition temperature reported in the literature(7) for cholesteryl cinnamate is 156° for the solid-cholesteric transition and 197° for the cholesteric-isotropic transition. In the present study the transition temperatures obtained are, for solid-cholesteric transition 160.5 °C and for cholesteric-isotropic transition 215 °C. This may be due to the purity of the sample and accuracy of the apparatus.

The first nine members of the present series exhibit enantiotropic cholesteric mesophases. The higher members starting with choles-

TABLE 1 Cholesteryl trans-*p*-*n*-alkoxy cinnamates:



R	Transition Temperatures (°C)			
	Smectic$_{II}$	Smectic$_{I}$	Cholesteric	Isotropic
—	—	—	160.5	215.0
CH_3	—	—	173.0	292.5
C_2H_5	—	—	152.0	293.5
C_3H_7	—	—	146.0	280.0
C_4H_9	—	—	134.0	281.0
C_5H_{11}	—	—	128.0	268.0
C_6H_{13}	—	—	128.5	262.5
C_7H_{15}	—	—	142.5	254.0
C_8H_{17}	—	—	144.0	249.0
C_9H_{19}	—	—	142.5	244.0
$C_{10}H_{21}$	133.0	158.5	167.0	238.5
$C_{12}H_{25}$	133.0	178.0	181.5	226.5
$C_{16}H_{33}$	—	107.0	181.5	200.0
$C_{18}H_{37}$	—	108.0	167.0	186.0

teryl-(trans-*p*-*n*-decyloxy) cinnamate exhibit polymesomorphism, i.e. smectic and cholesteric mesophases. It is interesting to note that cholesteryl-(trans-*p*-*n*-decyloxy) cinnamate and cholesteryl (trans-*p*-*n*-dodecyloxy) cinnamate exhibit an additional smectic mesophase. The cholesteric mesophase persists up to the last member of the series. When the transition temperatures are plotted against the number of carbon atoms in the alkyl chain, the transition points relating to the change cholesteric-isotropic fall on two falling curves, one representing the esters with an odd number of carbon atoms in the alkyl chain and the other representing the esters with an even number of carbon atoms in the alkyl chain. The latter curve lies above the former one. The smectic-cholesteric transition points lie on a smooth rising curve which rises to a maximum with the dodecyloxy ester at 181.5 °C and then falls off through the hexadecyloxy ester at 181.5 °C and the octadecyloxy ester at 167.0 °C, the maximum may probably be at C_{14}; whereas in the cholesteryl-*p*-*n*-alkoxy benzoates[8] it rises to a maximum with the dodecyloxy ester and then falls off through the hexadecyloxy and octadecyloxy esters. The smectic-cholesteric transition temperature curve does not coincide with the falling cholesteric-isotropic transition temperature curve. In all the acid ester series of cholesterol studied, the cholesteric mesophase persists up to the last member of the series, which is not the case with other homologous series exhibiting smectic

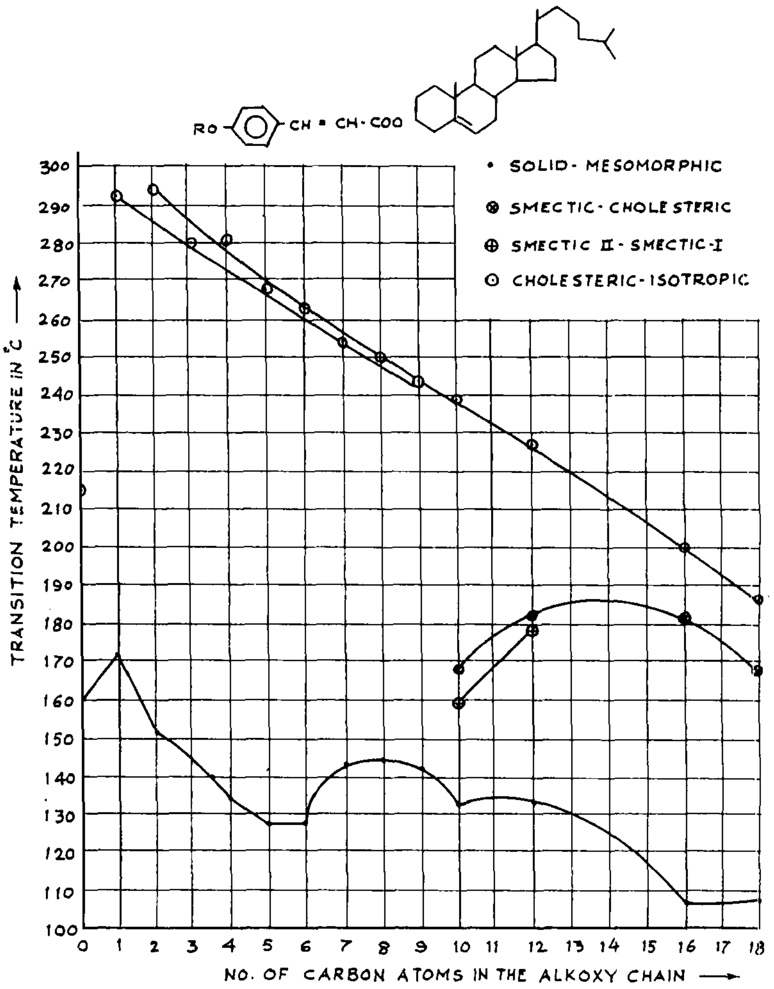


Figure 1.

and nematic mesophases except some stray cases.(9,10) The series other than cholesteryl compounds studied so far, comprise of rod-like straight molecules. Very little is known about the effect of broad and flat molecules on the smectic-nematic mesophase. It is possible that the cholesteryl compounds, due to its flatness and size, may maintain its parallel orientation even up to the last member, so that, on heating, it does not pass directly to the isotropic melt but exhibits a cholesteric mesophase along with the smectic mesophase.(11a,11b) When the compound is heated in the heating block and observed under the microscope, a focal-conic cholesteric phase is observed which even on slight disturbance changes to a plain cholesteric texture exhibiting vivid colours. All the compounds of the present series display different colours of the spectrum when observed through the microscope. In some compounds the colour is specific to the temperature. At the juncture of the smectic-cholesteric transition temperature a colour spectrum is observed, both while heating and cooling. The last members of the series also exhibit colour behavior which is not the case with *p*-*n*-alkanoates and *p*-*n*-alkoxy benzoates of cholesterol. This may be due to the presence of double bond in the cholesteryl cinnamates.

In Table 2 are summarized the thermal stabilities of the present series (*A*) and these are compared with those of the *p*-*n*-alkanoates of cholesterol (*B*), and *p*-*n*-alkoxy benzoates of cholesterol (*C*). It can be seen from Table 2 that the thermal stabilities of the mesophases of the present series (*A*) are much higher than those of the *p*-*n*-alkanoates of cholesterol (*B*). This increase in the thermal stabilities of the present series is expected, as the present series contains a phenyl ring and —CH=CH-group, which contribute to the increase in the polarisability and the length of the molecule.

TABLE 2

Average transition temperatures in °C.	'A'	'B'	'C'
Cholesteric-Isotropic (C_1–C_{10})	265.3	99.3	237.0
Smectic-Cholesteric (C_{10},C_{12},C_{16},C_{18})	174.2	79.5 (Monotropic) (C_{11},C_{13},C_{15},C_{17})	172.1

In the *p*-*n*-alkanoates series the smectic mesophase commences from the heptanoate as a monotropic phase, whereas in the present series it commences from the decyloxy ester as an enantiotropic smectic phase. This may be attributed to the polarisability of the phenyl ring and the presence of the —CH=CH-group which increases breadth of the molecule. It is difficult to postulate the commencement of the smectic phase in a homologous series. It commences later in series (*A*) than series (*B*), though thermally (*A*) is more stable. The high polarisability of the molecule increases the thermal stability of the mesophase, whereas increase in the breadth will reduce intermolecular cohesive forces which may reduce the thermal stability of the smectic mesophase and may affect the commencement of the smectic mesophase in a potentially mesomorphic homologous series. In the *p*-*n*-alkoxy benzoic acid series(12) the smectic mesophase commences from the heptyloxy derivative, whereas in the trans-*p*-*n*-alkoxy cinnamic acid series(13) the smectic mesophase commences from the nonyloxy derivative, even though the overall thermal stability of trans-*p*-*n*-alkoxy cinnamic acid series is higher than that of the *p*-*n*-alkoxy benzoic acid series. The two series differ by a —CH=CH-group. The commencement of the smectic mesophase in the cholesteryl-*p*-*n*-alkoxy benzoate series is from the heptyloxy derivative, whereas in the cholesteryl (trans-*p*-*n*-alkoxy) cinnamate series the smectic mesophase commences from the decyloxy ester. Here also the difference in the two series is the —CH=CH-group which contributes towards the breadth and polarisability of the series (*A*).

Gray(9,14) in his study of different mesomorphic homologous series has concluded that increase in the breadth has more pronounced effect on the smectic mesophase than on the nematic mesophase. Opinions are divided as to whether the cholesteric mesophase should be regarded as a modification of the smectic mesophase or of the nematic mesophase, or whether it is best to regard it as a third and separate type of mesophase.(15) If the cholesteric mesophase be considered as a modified smectic mesophase, then the breadth of the molecule should have almost the same effect on cholesteric and smectic mesophases. Recently the cholesteric mesophase (5,6b,6c) has been considered as a special type of the nematic mesophase. In that case the breadth of the molecule should have less pronounced effect on cholesteric mesophase than the smectic mesophase.

Table 2 shows that the cholesteric thermal stability of the present series (*A*) is greater than that of series (*C*), whereas the smectic thermal stability of the two series are very nearly the same. In the case of series (*A*) and (*B*), the increase in cholesteric thermal stability of series (*A*) is 166 °C, whereas the increase in the smectic thermal stability is 94.7 °C, which is less than the former one. These results indicate that the breadth has less effect on the cholesteric mesophase, whereas it has a pronounced effect on the reduction in the thermal stability of the smectic mesophase. It can thus be seen from the above discussion that the effect of the constitution on the cholesteric mesophase is similar to that on a nematic mesophase and that the cholesteric mesophase may be considered a special type of the nematic mesophase rather than the smectic one. A detailed study of more such homologous series should throw more light on the subject and help in arriving at some definite conclusion about the effect of structure and chemical constitution on the cholesteric mesophase.

Experimental

DETERMINATION OF TRANSITION TEMPERATURES

The melting points and transition temperatures of cholesteryl esters were determined with the help of a Leitz Ortholux Polarising Microscope equipped with a heating stage. The slides were prepared by heating the substance up to its mesomorphic temperature and putting a cover-slip over it and cooling.(8) The slides were then heated in the slot of the heating block of the microscope and the temperatures were noted. The temperature was raised gradually and within the critical region of the transition temperature to be noted, the heating was regulated to two degrees per minute. In this type of the slide, on heating, generally the focal conic cholesteric texture gives the plane cholesteric texture. The change from plane cholesteric texture to isotropic transition can be easily observed due to the high birefringence and colourful plane texture of the cholesteric phase.

PREPARATION OF COMPOUNDS

(1) *p*-*n*-Alkoxybenzaldehydes and trans-*p*-*n*-alkoxy cinnamic acids were prepared by the method of Gray.(13) Boiling points and transition temperatures compare well with the literature.

(2) Preparation of trans-*p*-*n*-alkoxy cinnamoyl chlorides:

Trans-*p*-*n*-alkoxycinnamoyl chlorides were prepared by treating the corresponding trans-*p*-*n*-alkoxy cinnamic acid with thionyl chloride (25% excess) and heating on a water bath till evolution of hydrochloric acid gas ceases. Excess of thionyl chloride is distilled off.

(3) Preparation of cholesteryl trans-*p*-*n*-alkoxy cinnamates:(2)

Stoichiometric amounts (0.01 mole) of cholesterol and trans-*p*-*n*-alkoxy cinnamoyl chloride were taken in a round-bottomed flask with N,N-dimethylaniline (20 ml) and heated at 120 °C in an oil bath for two hours. The mass was then added to ice cold water and the oily ester formed separates out; it was filtered, washed with acetone, dried and recrystallised from chloroform-acetone (1 : 1). The melting points and transition temperatures are given in Table 1. The analytical data are recorded in Table 3.

TABLE 3 Cholesteryl (trans-*p*-*n*-alkoxy) cinnamates:

	Required %		Formula	Found %	
R =	C	H		C	H
—	83.75	10.08	$C_{36}H_{52}O_2$	83.60	9.92
CH_3	81.32	9.87	$C_{37}H_{54}O_3$	81.12	9.88
C_2H_5	81.43	10.00	$C_{38}H_{56}O_3$	81.64	9.99
C_3H_7	81.52	10.10	$C_{39}H_{58}O_3$	81.55	9.83
C_4H_9	81.62	10.21	$C_{40}H_{60}O_3$	81.83	10.16
C_5H_{11}	81.74	10.30	$C_{41}H_{62}O_3$	81.66	10.48
C_6H_{13}	81.81	10.39	$C_{42}H_{64}O_3$	81.85	9.92
C_7H_{15}	81.91	10.47	$C_{43}H_{66}O_3$	81.02	10.51
C_8H_{17}	81.98	10.55	$C_{44}H_{68}O_3$	82.10	10.65
C_9H_{19}	82.08	10.64	$C_{45}H_{70}O_3$	82.08	10.51
$C_{10}H_{21}$	82.13	10.71	$C_{46}H_{72}O_3$	81.78	10.35
$C_{12}H_{25}$	82.28	10.86	$C_{48}H_{76}O_3$	82.02	10.43
$C_{16}H_{33}$	82.54	11.11	$C_{52}H_{84}O_3$	82.31	11.18
$C_{18}H_{37}$	82.66	11.23	$C_{54}H_{88}O_3$	82.41	11.22

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REFERENCES

1. Friedel, G., *Ann. Phys. (Paris)* **18**, 273 (1922).
2. Gray, G. W., *J. Chem. Soc.*, 3733 (1956).
3. Maidachenko, G. G. and Chistyakov, I. G., *Zh. Obshch. Khim.*, **37(8),** 1730 (1967).
4. Muller, J. H., U.S. Dept. Comm. AD. 634627 (1966); *C.A.* **66,** 119631j (1966).
5. Sackmann, E. *et. al.*, *J. Am. Chem. Soc.* **90,** 3567 (1968).
6. (a) Mme Leclercq, M., Billard, J. and Jaques, J., *Compt. Rend.* **266,** 654 (1968); (b) Mme Leclercq, M., Billard, J. and Jacques, J., *Mol. Cryst. and Liq. Cryst.* **8,** 367 (1969); (c) Gray, G. W., *Mol. Cryst. and Liq. Cryst.* **7,** 127 (1969).
7. Bragg, W., *Nature* **133,** 456 (1934).
8. Dave, J. S. and Vora, R. A., "Liquid Crystals and Ordered Fluids", Plenum Press, New York, 477 (1970).
9. Gray, G. W., Hartley, J. B., Ibbotson, A. and Jones, B., *J. Chem. Soc.*, 4359 (1955).
10. Dave, J. S. *et. al.*, unpublished work.
11. (a) Bernal, J. D. and Crowfoot, D., *Trans. Faraday Soc.* **29,** 1016 (1933); (b) Gray, G. W. and Jones, B., *J. Chem. Soc.*, 2556 (1954).
12. Gray, G. W. and Jones, B., *J. Chem. Soc.*, 4179 (1953).
13. Gray, G. W. and Jones, B., *J. Chem. Soc.*, 1467 (1954).
14. Gray, G. W., *J. Chem. Soc.*, 552 (1958).
15. Gray, G. W., "Molecular Structure and the properties of Liquid Crystals." Academic Press, 190 (1962).