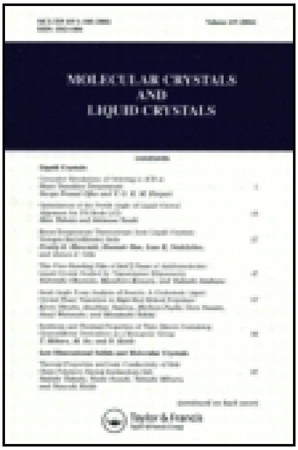

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Mesomorphic Behaviour of Cholesteryl Esters -VI: 4-n-Alkoxy-1-naphthylidence-p-aminobenzoates of Cholesterol

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Mesomorphic Behaviour of Cholesteryl Esters—VI:

4-*n*-Alkoxy-1-naphthylidene-*p*-aminobenzoates of Cholesterol†

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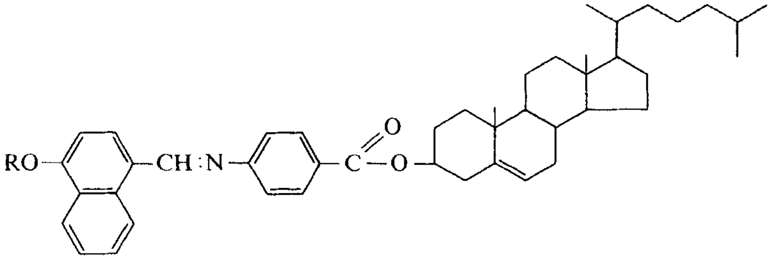
A homologous series of fourteen Schiff base compounds of the following type was prepared by condensing 4-*n*-alkoxy-1-naphthaldehydes with cholesteryl *p*-aminobenzoate, and its mesomorphic behaviour was studied.



$R = C_1–C_{18}$

All the members of the series exhibit enantiotropic cholesteric mesomorphism having good phase length and thermal stability. The smectic mesophase begins with the dodecyl derivative as a monotropic phase, becomes enantiotropic with the tetradecyl homolog, and continues to be enantiotropic through the octadecyl derivative. The cholesteric-isotropic transition temperatures lie on a generally falling curve which shows a distinct odd–even effect for the first five members only. The smectic–cholesteric transition curve rises steeply but does not merge with the falling cholesteric–isotropic transition curve. All the compounds give the cholesteric focal conic texture which on slight disturbance changes to the plane texture. The smectic phase has a focal conic texture.

For the initial members of the series the cholesteric–isotropic transitions are not precisely reversible as these compounds begin to decompose near their cholesteric–isotropic transition point. The polymesomorphic compounds exhibit a colour change at the smectic–cholesteric

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transition both while heating and cooling. No blue phase is observed when the isotropic liquid is cooled.

The thermal properties of the series are compared with those of the other related homologous series.

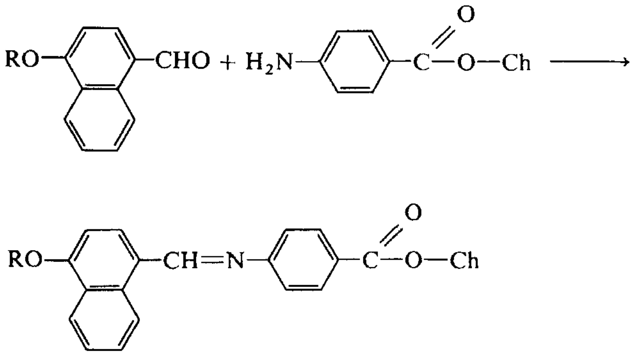
INTRODUCTION

Homologous series are studied to correlate mesomorphic behaviour with structural variations in the molecules of the compounds. Compared to the cholesterogenic homologous series, many nematogenic and smectogenic homologous series of different molecular structures have been studied. The cholesterogenic compounds include both steroids and non-steroids. Gray[1] studied the mesomorphic behaviour of a homologous series of *n*-alkanoates of cholesterol. Since then a number of homologous series of the esters of cholesterol have been reported.[2–9] In these studies the 3β-substituents of cholesterol are mainly aliphatic. In addition, a few studies on aryl esters of cholesterol have been reported.[10–13]

Dave *et al.*[14,15] have studied the effects resulting from the introduction of naphthalene moieties into a number of nematogenic systems. To investigate the comparable effect of a naphthalene moiety inserted into a cholesteric system, we prepared and investigated the homologous series of 4-*n*-alkoxy-1-naphthylidene-*p*-aminobenzoates of cholesterol.

RESULTS AND DISCUSSION

A homologous series of fourteen Schiff base esters was prepared by the following synthetic route:



R = C_1–C_{18} Ch = Cholesteryl

TABLE I

Cholesteryl 4-*n*-alkoxy-1-naphthylidene-*p*-aminobenzoates
$RO \cdot C_{10}H_6 \cdot CH{:}N \cdot C_6H_4 \cdot CO_2 \cdot C_{27}H_{45}$

n-Alkyl group (R)	Transition temperatures in °C		
	Solid–smectic	Solid–cholesteric or smectic–cholesteric	Cholesteric–isotropic
Methyl	—	205.5	305.0
Ethyl	—	198.5	312.0
Propyl		182.0	304.0
Butyl	—	165.5	303.5
Pentyl	—	173.5	298.5
Hexyl	—	163.5	296.0
Heptyl	—	162.5	290.0
Octyl	—	159.5	285.5
Nonyl	—	149.5	279.0
Decyl	—	139.0	274.0
Dodecyl	(122.5)	140.0	266.5
Tetradecyl	110.0	145.0	256.0
Hexadecyl	124.0	165.0	247.0
Octadecyl	94.5	187.5	237.0

Value in parenthesis indicates monotropy

The melting points and transition temperatures are summarized in Table I. All the members of the homologous series exhibit enantiotropic cholesteric mesomorphism and show good phase length and thermal stability. The smectic mesophase begins with the dodecyl derivative as a monotropic phase, becomes enantiotropic with tetradecyl homolog and continues to be enantiotropic through the octadecyl derivative.

When the transition temperatures are plotted against the number of carbon atoms in the alkoxy chain, the cholesteric–isotropic transition points lie on a generally falling curve which exhibits an odd–even effect for the first five members. The smectic curve rises steeply but does not merge with the falling cholesteric–isotropic curve, or at least not within the range of homologous members investigated here (Figure 1).

When the cholesteric compound is studied under the microscope, the solid first melts to a cholesteric phase with a focal conic texture which on slight disturbance changes to the plane texture with bright oily streaks. This on further heating changes to the isotropic liquid. In the initial members the cholesteric–isotropic transition points are not exactly reversible because these compounds slowly begin to decompose at the transition temperatures. It should be mentioned here that the non-reversibility of the cholesteric-isotropic transitions in these cases is not because of the blue phase as observed by Coats and Gray[16] in some cholesteryl esters.

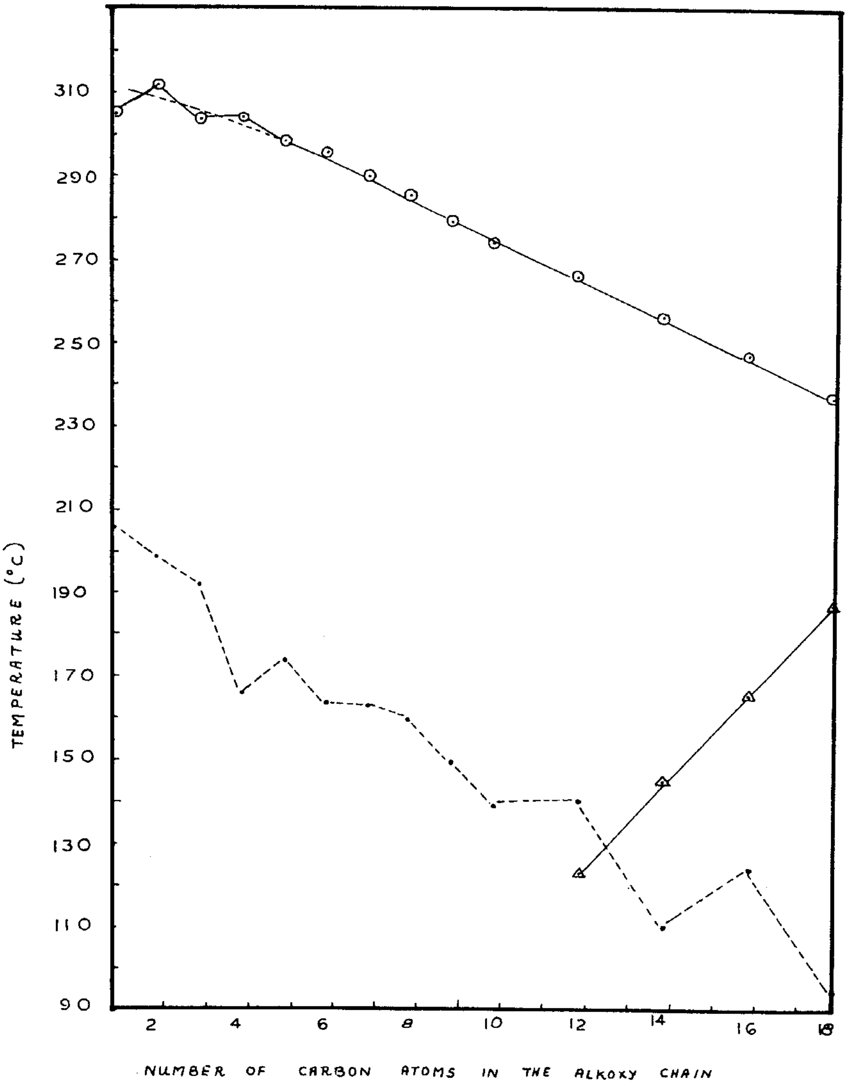


FIGURE 1 Cholesteryl 4-*n*-alkoxy-1-naphthylidene-*p*-aminobenzoates.
•– – – •, solid–mesomorphic; △——△, smectic–cholesteric; ⊙——⊙, cholesteric–isotropic.

In polymesomorphic compounds the solid melts to a smectic phase with a focal conic texture. This on further heating gives the cholesteric phase. No homeotropic smectic phase is observed. The cholesteric phase has a focal conic texture which on slight disturbance gives the cholesteric plane texture with bright oily streaks. On further heating the cholesteric phase changes to the isotropic liquid. The isotropic liquid on cooling gives the cholesteric phase with the focal conic texture which on disturbance changes to the cholesteric plane texture. The cholesteric phase appears one or two degrees below the cholesteric–isotropic transition temperature due to the slight decomposition of the compounds at the transition points. The cholesteric phase on cooling gives a smectic phase with focal conic texture. The polymesomorphic compounds exhibit a colour change at the smectic–cholesteric transition both while heating and cooling.

Table II summarizes the average thermal stabilities and commencement of the smectic phase in the homologous

4-*n*-Alkoxy-1-naphthylidene-*p*-aminobenzoates of cholesterol (A)

and compares these with those of:

p-*n*-alkoxybenzylidene *p*′-aminobenzoates of cholesterol[12] (B)

6-*n*-alkoxy-2-naphthoates of cholesterol[12] (C)

4-*n*-alkoxy-2-naphthoates of cholesterol[11] (D)

p-*n*-alkoxybenzoates of cholesterol[11] (E)

The geometry of these series is given in Figure 2.

The cholesteric and smectic thermal stabilities of series B are higher than those of series A. Molecules of series A and B have the same molecular structure except that the molecules of series A contain the 1,4-substituted naphthalene nucleus at the alkoxy end of the molecules in place of the benzene ring in the corresponding position in the molecules of series B.

TABLE II

Average thermal stabilities in °C

Series	A	B	C	D	E
Cholesteric–isotropic (C_1–C_{18})	282.4	305.8	267.0	157.9	222.4
Smectic–cholesteric (C_{12}–C_{18})	155.0	256.4	220.0	98.8	173.2
Commencement of smectic phase	C_{12}	C_7	C_5	C_{12}	C_7

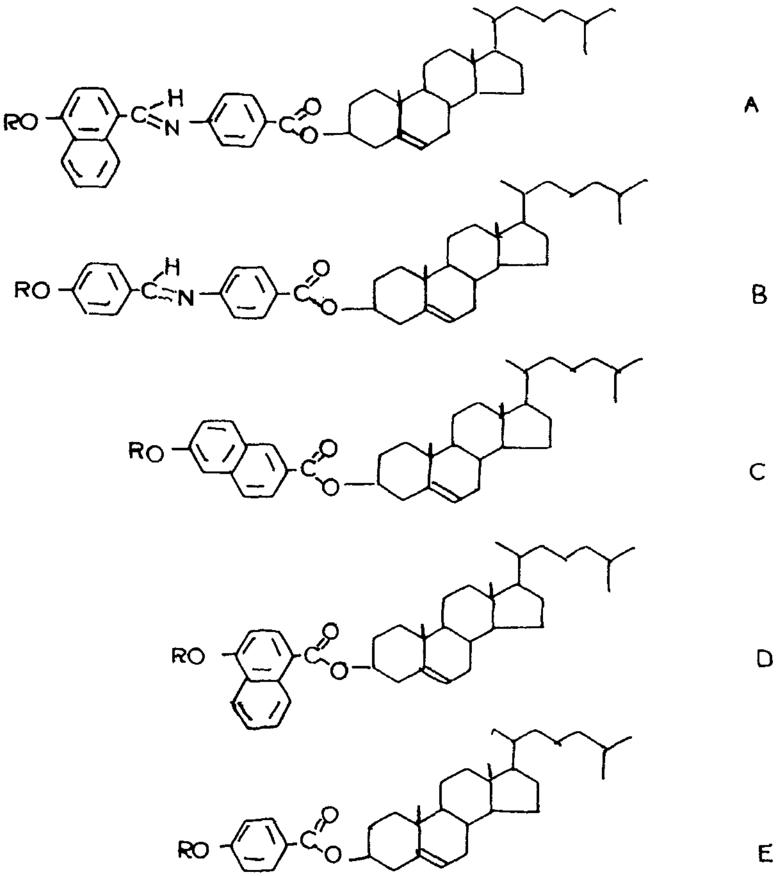


FIGURE 2

The reduction in the thermal stabilities of series A can thus be ascribed to the increased breadth of the molecules of series A. The 1,4-substituted naphthalene nucleus can be considered as a benzene ring with a side substituent bridging the positions 2 and 3. Gray has pointed out that the increase in breadth of the molecules reduces both nematic and smectic thermal stabilities, and the effect is more pronounced on the smectic mesophase.[17] Dave *et al.*[14,15] have observed the same behaviour in a number of nematogenic naphthalene Schiff base compounds. All the materials studied in the series demonstrate the same behaviour; their smectic thermal stability is more depressed than their cholesteric thermal stability. This behaviour provides an evidence that the cholesteric phase is akin to the nematic phase.

Series A and C provide another interesting comparison. The cholesteric thermal stability of series A is higher than that of series C, whereas the smectic thermal stability of series A is lower than that of series C. Molecules of series A possess a 1,4-substituted naphthalene moiety, a benzene ring, and a —CH=N— group in place of a naphthalene nucleus with 2,6-substitution in the molecules of series C. The molecules of series A will thus be longer and more polarized than those of series C, and the increase in cholesteric thermal stability of series A can be explained. Compared against 2,6-substitution in molecules of series C, the breadth of the molecules of series A—due to the 1,4-substitution at the naphthalene nucleus—is considerably increased and thus the smectic thermal stability is more affected than the cholesteric thermal stability as mentioned before. Indeed, the smectic thermal stability of series A is considerably lower than that of series C.

The thermal stabilities of series A are higher than those of series D, the increase being less in the case of the smectic thermal stability. The molecules of both series A and D contain a 1,4-substituted naphthalene moiety but the molecules of series A contain a benzene ring and an azomethine group more than the molecules of series D, which make the molecules of series A longer and more polarized. The increase in the length and polarizability of the molecules of series A should increase both the thermal stabilities of series A to the same extent, but the breadth in the molecules of series A will have an adverse effect on the smectic thermal stability, and so the smectic thermal stability will not increase to the same extent as the cholesteric thermal stability. Thus the increase in the smectic thermal stability of series A is less compared with the cholesteric thermal stability.

Compared with series E, the molecules of series A are longer by a 1,4-substituted naphthalene nucleus and a —CH=N— group. The molecules of series A will thus be longer and more polarized than those of series E, and so the cholesteric thermal stability of series A is increased but the molecules of series A, possessing a 1,4-substituted naphthalene nucleus are broader than those of series E; therefore, the smectic thermal stability of series A is reduced and actually becomes less than that of series E.

The smectic mesophase appears rather late in this series at the C_{12} derivative. Since molecules of series B are less broad than those of series A, the smectic mesophase begins already with the 7th homolog. In series C the smectic phase appears rather early at C_5 derivative. Molecules of series C contain 2,6-substituted naphthalene moiety which will contribute linearity and polarizability to the molecules; the smectic mesophase therefore, commences with the C_5 member. In series D the smectic mesophase appears late as C_{12} derivative. This series contains a 1,4-substituted naphthalene nucleus which makes the molecules of series D considerably broad and thereby delays the appearance of the smectic mesophase. In the case of series E the smectic phase appears from the C_7 homologue. Compared to the present series this series is less broad and so the smectic phase appears early at the C_7 member.

EXPERIMENTAL

A Determination of transition temperatures

Preliminary measurements were made by the optical method of Dave and Dewar.[18] The precise measurements were, however, made with a Leitz Ortholux polarizing microscope as described elsewhere.[12]

B Preparation of Compounds

p-Aminobenzoate of cholesterol[12] (0.002 mol), 4-*n*-alkoxy-1-naphthaldehydes[14] (0.0022 mol) and nitrobenzene (A.R. grade) were taken in a round bottom flask (50 ml) fitted with an air condenser. The contents of the flask were heated gently for about one hour. The crude product obtained on cooling was boiled with enthanol and filtered. The residue was then dissolved in chloroform and charcoalized. The product was crystallized from a chloroform-methanol (1 : 1) mixture to constant melting point and transition temperatures. All compounds crystallized as yellow flakes. The melting points and transition temperatures are given in Table I. The analytical data are given in Table III. Yield about 60 percent.

TABLE III

Cholesteryl 4-*n*-alkoxy-1-naphthylidene-*p*-aminobenzoates

$RO \cdot C_{10}H_6 \cdot CH:N \cdot C_6H_4 \cdot CO_2 \cdot C_{27}H_{45}$

n-Alkyl group (R)	Molecular formula	% Required			% Found		
		C	H	N	C	H	H
Methyl	$C_{46}H_{59}O_3N$	81.98	8.82	2.08	82.15	8.84	2.20
Ethyl	$C_{47}H_{61}O_3N$	82.06	8.94	2.03	82.26	8.97	1.94
Propyl	$C_{48}H_{63}O_3N$	82.10	9.05	2.00	81.64	8.70	2.10
Butyl	$C_{49}H_{65}O_3N$	82.21	9.15	1.96	82.60	8.91	2.29
Pentyl	$C_{50}H_{67}O_3N$	82.24	9.25	1.92	82.22	9.31	1.78
Hexyl	$C_{51}H_{69}O_3N$	82.31	9.35	1.88	82.15	9.54	1.90
Heptyl	$C_{52}H_{71}O_3N$	82.35	9.44	1.85	82.24	9.22	1.67
Octyl	$C_{53}H_{73}O_3N$	82.43	9.53	1.82	82.30	9.55	1.75
Nonyl	$C_{54}H_{75}O_3N$	82.49	9.62	1.78	82.43	9.83	1.73
Decyl	$C_{55}H_{77}O_3N$	82.52	9.70	1.75	82.54	9.81	1.55
Dodecyl	$C_{57}H_{81}O_3N$	82.68	9.86	1.69	83.07	9.91	1.82
Tetradecyl	$C_{59}H_{85}O_3N$	82.73	10.00	1.64	82.58	9.64	1.81
Hexadecyl	$C_{61}H_{89}O_3N$	82.85	10.14	1.58	83.16	10.28	1.72
Octadecyl	$C_{63}H_{93}O_3N$	82.91	10.27	1.53	82.62	10.43	1.66

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