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J. S. Dave [a] & George Kurian [a]
[a] Chemistry Department, M.S. University of Baroda, Baroda, 2, India

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Mesomorphic Behaviour of Cholesteryl Esters: IV: *p*-*n*-Alkoxybenzylidene-*p*′-Aminobenzoates of Cholesterol†

J. S. DAVE and GEORGE KURIAN

Chemistry Department
M.S. University of Baroda
Baroda 2, India

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Abstract—Thirteen Schiff's base compounds have been prepared by condensing *p*-aminobenzoate of cholesterol with *p*-*n*-alkoxybenzaldehydes and their mesomorphic behaviour has been studied. All the members of this series are enantiotropic mesomorphic. The first six members are only cholesteric; the rest are polymesomorphic, i.e. smectic and cholesteric. The smectic phase increases with the increase in the alkyl chain length at the cost of the cholesteric phase. The cholesteric–isotropic transition temperatures lie on a generally falling curve which shows a distinct odd–even effect for the first five members. The smectic–cholesteric transition curve rises smoothly to a maximum and then falls off; it does not coincide 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 and shows iridescent colours. Just near the smectic–cholesteric transition temperature a colour change is observed both while heating and cooling. In the last members of the series the focal conic smectic texture turns to a homeotropic texture on heating. The mesophases of the cholesteryl *p*-*n*-alkoxybenzylidene-*p*′-aminobenzoates are thermally much more stable than those of the other series.

1. Introduction

Liquid crystalline properties of some esters of cholesterol have been reported before. Gray⁽¹⁾ studied the influence of alkyl chain length on the mesomorphic properties of the cholesteryl alkanoates. Dave and Vora^(2,3) studied the effect of arene substitution in the 3β position of cholesterol by preparing homologous series of *p*-*n*-alkoxybenzoates and trans-*p*-*n*-alkoxycinnamates of cholesterol. In an attempt to

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correlate the effect of changes in molecular structure and mesomorphic behaviour of aromatic esters of cholesterol, another homologous series was prepared. *p*-*n*-Alkoxybenzylidine-*p*′-aminobenzoates of cholesterol, comprising an azomethine (—CH=N—) group, were synthesized by condensing *p*-*n*-alkoxybenzaldehydes with cholesteryl *p*-aminobenzoate.

2. Results and Discussion

Thirteen esters of cholesterol were prepared. The melting points and the transition temperatures are compiled in Table 1. Cholesteryl-*p*-aminobenzoate itself is mesomorphic. All cholesteryl *p*-*n*-alkoxybenzylidene-*p*′-aminobenzoates have enantiotropic mesophases. The first six members exhibit only the cholesteric mesophase; the higher members, starting with the heptyloxy derivative, show both smectic and cholesteric mesophases. The cholesteric mesophase persists up to the last member of the series investigated. This is the common behaviour of all the cholesteryl ester series. This behaviour of the cholesteryl compounds can be attributed to the flat and broad cholesteryl moiety of these compounds.

When the transition temperatures are plotted against the number of carbon atoms in the alkyl chain, the cholesteric–isotropic transition

TABLE 1 Cholesteryl *p*-*n*-alkoxybenzylidene-*p*′-aminobenzoates: $RO.C_6H_4.CH{=}N.C_6H_4.CO_2.C_{27}H_{45}$

Alkyl group (R)	Transition temperatures in °C Solid–Smectic	Solid–Cholesteric or Smectic–Cholesteric	Cholesteric–Isotropic
Methyl	—	166.5	320.0
Ethyl	—	171.0	328.5
Propyl	—	169.5	323.5
Butyl	—	163.5	323.0
Pentyl	—	164.0	317.0
Hexyl	—	155.5	314.5
Heptyl	152.5	163.5	312.0
Octyl	153.5	189.5	308.0
Nonyl	137.5	206.0	305.0
Decyl	138.0	225.0	301.0
Dodecyl	142.5	250.5	294.0
Hexadecyl	107.0	260.0	278.0
Octadecyl	108.5	255.5	272.0

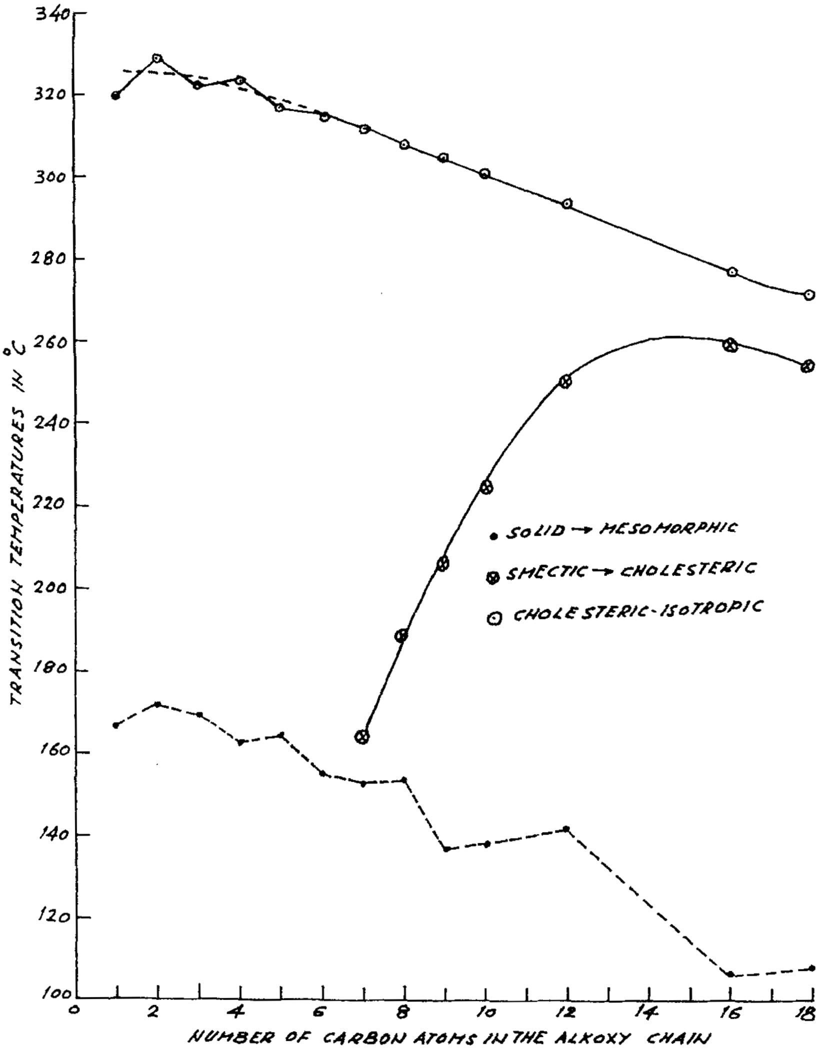


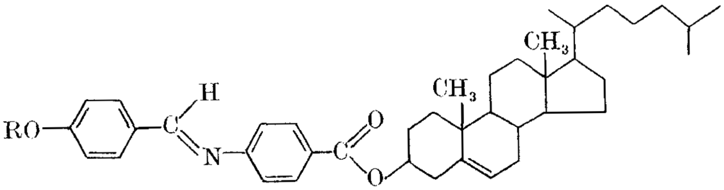
Figure 1. Cholesteryl *p*-*n*-alkoxybenzylidene *p′*-aminobenzoates.

points lie on one curve, generally falling, and showing a distinct odd–even effect only for the first five members (Fig. 1). The smectic–cholesteric transition points lie on a steep rising curve which probably has its maximum in the not investigated tetradecyloxy ester.

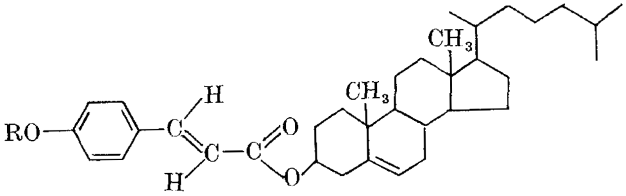
In the case of cholesteryl *p*-*n*-alkoxybenzoates, the smectic–cholesteric transition curve rises to a maximum at dodecyloxy ester and in the case of cholesteryl trans-*p*-*n*-alkoxycinnamates it is at the tetradecyloxy ester. The smectic–cholesteric transition curve does not coincide with the falling cholesteric–isotropic transition temperature curve.

Table 2

Average transition temperature in °C	A	B	C	D
Cholesteric–Isotropic (C_1–C_6)	321.1	279.5	250.8	100.1
Smectic–Cholesteric (C_{10}, C_{12}, C_{16}, C_{18})	247.7	174.2	172.1	79.7
Commencement of the smectic mesophase	heptyl	decyl	heptyl	heptanoate



A



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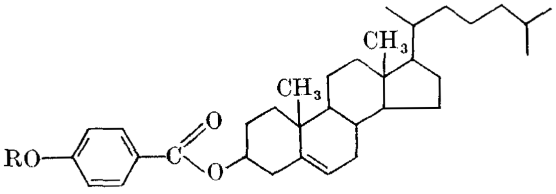

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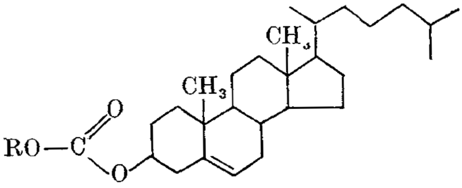

D

When a suitable cholesteric compound is heated and observed under the microscope it melts to a cholesteric mesophase with a focal conic texture, which even on slight mechanical disturbance changes to a plane cholesteric texture and shows iridescent colours. This is also the behaviour when a smectic mesophase precedes the cholesteric. Usually just near the smectic–cholesteric transition temperature, a colour change is observed both while heating and cooling.

Table 2 summarizes the average thermal stabilities of mesophases of the present series (A), trans-*p*-*n*-alkoxycinnamates of cholesterol (B),⁽³⁾ *p*-*n*-alkoxybenzoates of cholesterol (C)⁽²⁾ and cholesteryl alkanoates (D).⁽¹⁾ It can be seen that the stability of the mesophases of the present series is much higher than that of the cholesteryl alkanoates (D). This is expected as the present series contains two phenyl rings with an azomethine group inserted, all contributing to the increase in the polarizability and the length of the molecule in series (A). The molecular structures of the series are also presented in Table 2.

The mesophases of series (A) are also thermally more stable than those of series (B) and (C). This behaviour can be attributed to the increased length and polarizability of the molecules of the present series. Generally, an increase in the length of the molecule of a potentially mesomorphic compound increases the overall thermal stability provided that it also increases the polarizability of the molecule. Thus by the addition of a unit, such as a benzene ring to the molecule of a mesomorphic compound, the thermal stability of both smectic and nematic mesophases will increase as long as the molecule is not broadened.⁽⁴⁾ In the present series the thermal stabilities of both the smectic and cholesteric mesophases are higher than those of series (B), (C) and (D). This indicates that the effect of chemical constitution on a cholesteric mesophase of a mesomorphic compound is similar to that on a nematic mesophase.

In a potentially mesomorphic series the first few members are usually only nematic or cholesteric. With the lengthening of the alkyl chain the smectic mesophase makes its appearance in the middle members. The exact commencement of the smectic mesophase is rather difficult to postulate. Although a high polarizability of the molecule increases the thermal stability of the mesophases, an increase in the breadth will reduce intermolecular cohesive forces.

Thus the thermal stability of the smectic mesophase may be reduced and the commencement of the smectic mesophase in a mesomorphic homologous series may be delayed.

In the present series, the smectic mesophase commences at the heptyloxy ester, which is earlier than that in series (B). The cholesteryl *p*-*n*-alkoxybenzylidene-*p*′-aminobenzoates contain one more benzene ring and a —CH=N— group in place of —CH=CH— group in series (B). This increases the length and the polarizability of the molecule without apparent change in the breadth. Thus the higher thermal stability and early commencement of the smectic mesophase can be understood. It is interesting to note that the commencement of the smectic mesophase in the present series coincides with that in series (C). The molecules of the present series are longer by a benzene ring and have an azomethine (—CH=N—) group which adds to the polarizability. In fact, the commencement of the smectic mesophase in the cholesteryl *p*-*n*-alkoxybenzylidene-*p*′-aminobenzoates should be earlier than in series (C). But the azomethine group might cause some difficulty in the close packing of the molecules, and this may be the reason for the delay in the commencement of the smectic mesophase so that its start coincides with that in series (C).

In the case of cholesteryl alkanoates (series D) the smectic mesophase commences at the heptanoate. The fact that the smectic mesophase does not start earlier in the homologous series of cholesteryl *p*-*n*-alkoxybenzylidene-*p*′-aminobenzoates indicates that the azomethine group and the benzene ring indeed make the close packing of the molecules comparatively difficult. Thus the commencement of the smectic mesophase is delayed despite the increase in length and polarizability of the molecule.

3. Experimental

DETERMINATION OF TRANSITION TEMPERATURES

Preliminary measurements were made by the optical method of Dave and Dewar.(5) The precise measurements were, however, made with a polarizing microscope. To prepare the slide, the specimen was heated up to its mesomorphic temperature on a glass slide, and a coverslip was pressed down on the liquid to obtain a thin film of the material. The slide was then inserted in the slide slot of the hot stage fitted to the Leitz Ortholux polarizing microscope. In this electrically heated block, the sample could be observed continuously under carefully controlled temperature. In the neighbourhood of each phase transition the temperature was raised at the rate of 0.5 °C per minute. Temperatures for various transitions were recorded by standard thermometers. The transitions were also checked by lowering the temperature slowly and observing the phase changes. As cholesteryl *p*-*n*-alkoxybenzylidene-*p*′-aminobenzoates begin to decompose near the cholesteric–isotropic transition temperature, this change was not precisely reversible on cooling. Fresh slides were used every time to determine the transitions.

Preparation of Compounds

p-*n*-Alkoxybenzylidene-*p*′-aminobenzoates of cholesterol were prepared by condensing *p*-*n*-alkoxybenzaldehydes with cholesteryl *p*-aminobenzoate. The cholesteryl *p*-aminobenzoate was obtained by the reduction of *p*-nitrobenzoate of cholesterol. *p*-*n*-Alkoxybenzaldehydes were prepared by the method of Gray.(6)

p-Nitrobenzoate of Cholesterol(7)

Cholesterol (5 g) and *p*-nitrobenzoyl chloride (3 g) were mixed with dry pyridine (10 ml) in a conical flask and slowly heated to boiling. The solution was allowed to cool and the separated cholesteryl *p*-nitrobenzoate was washed with a little alcohol to remove the pyridine. The crude product was dissolved in chloroform and filtered. On addition of acetone to the filtrate, cholesteryl *p*-nitrobenzoate precipitated. It was then recrystallized from ethyl methyl ketone yielding white plates.

M.P. 191.5–260.0 °C. Yield 70%.

p-Aminobenzoate of Cholesterol(7)

Cholesteryl *p*-aminobenzoate was prepared by the reduction of cholesteryl *p*-nitrobenzoate with iron powder and acetic acid. Cholesteryl *p*-nitrobenzoate (3 g) and glacial acetic acid (40 ml) were taken in a 150 ml round bottom flask fitted with a water condenser. The mixture was heated to boiling and iron powder (1.7 g; 100 mesh) was added little by little. After refluxing for three hours the mixture was cooled and filtered. The solid mass obtained was washed with 1 N hydrochloric acid until the washings were colourless. It was then washed with water until the washings were neutral to litmus. The crude product was dried and crystallized from isoamyl-acetate forming white needles.

M.P. 237.0–248.5 °C. Yield 46%.

p-*n*-ALKOXYBENZYLIDENE-*p*′-AMINOBENZOATES OF CHOLESTEROL

p-Aminobenzoate of cholesterol (1 mol) was mixed with *p*-*n*-alkoxybenzaldehyde (1.5 mol) and was heated in an oil bath at 160–170 °C for one hour. The product obtained was boiled with alcohol and filtered. It was dissolved in chloroform and treated with charcoal. The product was crystallized from ethyl methyl ketone to constant transition temperatures. All esters crystallized as white needles. The transition temperatures are given in Table 1. The analytical data is recorded in Table 3; Yield about 50%.

TABLE 3 Cholesteryl *p*-*n*-Alkoxybenzylidene-*p*′-Aminobenzoates

Alkyl group	Molecular formula	Percentage required			Percentage found		
		C	H	N	C	H	N
CH_3	$C_{42}H_{57}O_3N$	80.85	9.21	2.25	80.63	9.17	2.45
C_2H_5	$C_{43}H_{59}O_3N$	80.96	9.32	2.20	80.76	9.07	2.51
C_3H_7	$C_{44}H_{61}O_3N$	81.06	9.43	2.15	81.21	9.18	2.24
C_4H_9	$C_{45}H_{63}O_3N$	81.15	9.54	2.10	80.85	9.23	1.91
C_5H_{11}	$C_{46}H_{65}O_3N$	81.25	9.64	2.06	81.37	9.28	2.33
C_6H_{13}	$C_{47}H_{67}O_3N$	81.33	9.73	2.02	81.47	9.34	2.24
C_7H_{15}	$C_{48}H_{69}O_3N$	81.43	9.82	1.98	81.93	9.86	1.82
C_8H_{17}	$C_{49}H_{71}O_3N$	81.53	9.91	1.94	81.23	9.54	2.24
C_9H_{19}	$C_{50}H_{73}O_3N$	81.58	9.99	1.90	81.66	10.08	1.88
$C_{10}H_{21}$	$C_{51}H_{75}O_3N$	81.66	10.08	1.87	81.62	9.99	2.25
$C_{12}H_{25}$	$C_{53}H_{79}O_3N$	81.77	10.23	1.79	81.58	10.00	1.92
$C_{16}H_{33}$	$C_{57}H_{87}O_3N$	82.08	10.51	1.68	82.49	10.55	1.90
$C_{18}H_{37}$	$C_{59}H_{91}O_3N$	82.17	10.64	1.62	82.02	10.44	1.76

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