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The Odd-Even Effect in Steryl ω-Phenylalkanoates†

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We became interested in the ω-phenylalkanoates of cholesterol after it was reported⁽¹⁾ that of the first five members investigated only the odd esters were mesomorphic, but not the even members cholesteryl phenylacetate and 4-phenylbutyrate. However, we found a cholesteric mesophase in cholesteryl 4-phenylbutyrate. We also observed that the temperature values of the cholesteric–isotropic transitions fell on two curves, with the odd-numbered members forming the higher branch, and the even-numbered members forming the lower branch. The two curves did not merge, and no smectic–cholesteric transitions were observed except in cholesteryl 8-phenyloctanoate, the last member studied in that investigation.(2)

A similar, but less pronounced, odd–even behavior has been reported(3) for the cholesteric–isotropic transition temperatures of the first 10 homologues of the S-cholesteryl alkanethioates. These alternations of transition temperatures are not limited to the cholesteric–isotropic case since they have also been reported for smectic–nematic and nematic–isotropic phase transitions.(4)

In order to compare the effects of structural changes on the odd–even effect in ω-phenylalkanoates of 3β-sterols, we synthesized and investigated the homologous series of 5α-cholestan-3β-yl ω-phenylalkanoates (I) and S-cholesteryl ω-phenylalkanethioates (II).

1. Preparation of Materials

The ω-**Phenylalkanoic Acids**(5,6,7) were obtained from the ester

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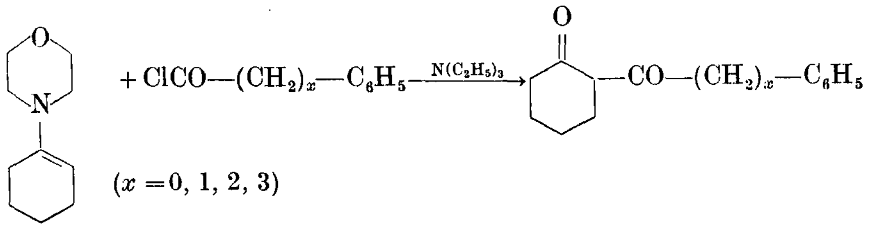
chlorides of α, ω-dicarboxylic acids and the corresponding dialkylcadmium compounds$^{(8,9)}$:

$$CH_3OOC—(CH_2)_x—COCl + Cd[(CH_2)_yC_6H_5]_2 \rightarrow$$

$$CH_3OOC—(CH_2)_x—CO—(CH_2)_y—C_6H_5 \xrightarrow[\text{Kishner}]{\text{Wolff-}} HOOC—(CH_2)_z—C_6H_5$$

or by chain elongation *via* enamines$^{(10)}$:

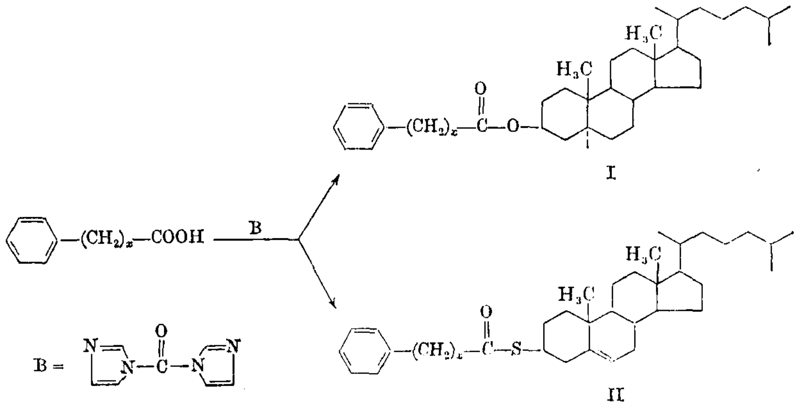


(x = 0, 1, 2, 3)

$$\xrightarrow{\text{KOH}} HOOC—(CH_2)_5—CO—(CH_2)_x—C_6H_5 \xrightarrow[\text{Kishner}]{\text{Wolff-}} HOOC—(CH_2)_{6+x}—C_6H_5$$

The purity was checked by gas chromatography of the corresponding methyl esters on EGSS-X (15%) and XE-61 (3%) phases, and found to be in the range of 99%.

The **Steryl Esters** were obtained by the reaction of the imidazolides of the ω-phenylalkanoic acids with the sterol under catalysis with sodium methoxide$^{(11,12)}$:



Because some of the side products formed in the esterification could not be removed by recrystallization, the compounds were chromatographed on silica gel. In each case the materials were uniform on thin-layer chromatography and satisfactory elemental analyses were obtained. Transition temperatures were determined and mesophases were identified under the microscope with a temperature-programmed Mettler FP II hot stage.(13) The temperature values are corrected.

2. 5α-Cholestan-3β-yl ω-Phenylalkanoates (I)

The homologous series of the ω-phenylalkanoates of 5α-cholestan-3β-ol exhibits a pronounced odd–even effect for the cholesteric–isotropic transition temperatures in analogy to the ω-phenylalkanoates of cholesterol(14) (Fig. 1). The two curves formed by the cholesteric–isotropic transition temperatures can be represented as hyperbolas with a deviation of only a few °C as in the case of the corresponding cholesteryl series. All odd members are monotropic cholesteric and their transition temperatures form the upper branch.

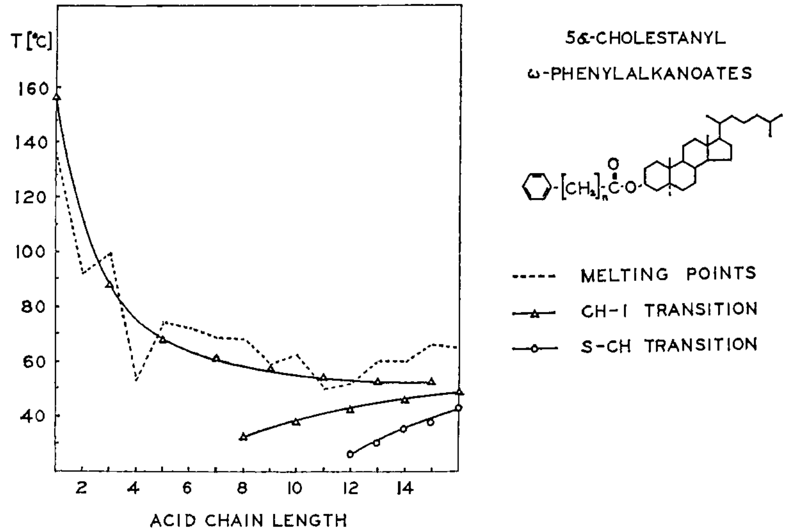


Figure 1. Transition points of 5α-cholestan-3β-yl ω-phenylalkanoates, - - - -, melting point; —△—, cholesteric–isotropic transition; —○—, smectic–cholesteric transition.

The 8-phenyloctanoate is the first even member exhibiting a monotropic cholesteric mesophase. This mesophase is not observed in the preceding members phenylacetate, 4-phenylbutyrate and 6-phenylhexanoate. Extrapolation of the lower branch indicates that the cholesteric–isotropic transitions can only be expected at a temperature far below that at which the isotropic melts crystallize on cooling. Cholesteric colors are exhibited by all mesomorphic members of this series. Smectic mesophases are observed only in the last five members, starting with the 12-phenyldodecanoate. The smectic–cholesteric transition temperatures do not exhibit an odd–even effect but increase almost linearly with chain length.

3. S-Cholesteryl ω-Phenylalkanethioates (II)

The phase transitions of the ω-phenylalkanoates of 3β-mercapto-cholest-5-ene (thiocholesterol) are presented in Fig. 2. The melting points show a regular behavior with the higher temperature values

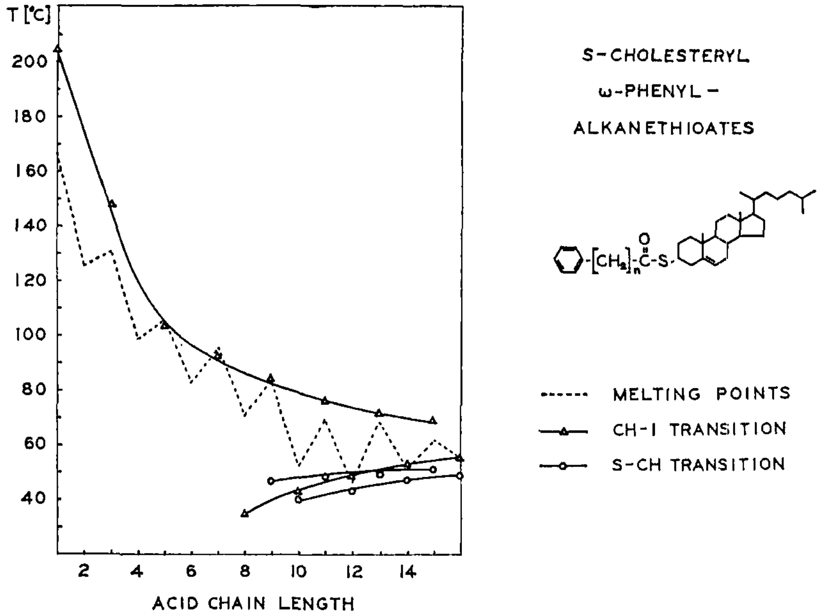


Figure 2. Transition points of S-cholesteryl ω-phenylalkanethioates. ----, melting point; —△—, cholesteric–isotropic transition; —○—, smectic–cholesteric transition.

for odd and the lower temperatures for even homologues. No other homologous series of steryl derivatives has exhibited such a regular temperature dependence of the melting points. The cholesteric–isotropic transition temperatures fall on two distinct branches: the high temperature branch for odd chain length and the low temperature branch for even chain length. The two curves again can be represented in close approximation as hyperbolas. The even members phenylthioacetate, 4-phenylthiobutyrate and 6-phenylhexanethioate do not exhibit cholesteric mesophases. All the other members of this series are monotropic cholesteric and most of them exhibit cholesteric colors. The smectic–cholesteric transition temperatures also show an odd–even effect of distinct regularity, a phenomenon never observed in any other homologous series of 3β-steryl derivatives. The high temperature branch is formed by the odd, and the low temperature branch by the even members of this series. However, the alternations are much smaller than in the cholesteric–isotropic phase transitions.

4. Summary and Conclusion

Figure 3 depicts the cholesteric–isotropic transition temperatures of the ω-phenylalkanoates of cholesterol,(2,14) 5α-cholestan-3β-ol, and 3β-mercaptocholest-5-ene. The transition temperatures of the 5α-cholestan-3β-yl derivatives are consistently lower than those of the corresponding cholesteryl analogues. In both homologous series the odd–even effect might disappear with approximately the 20th member. The extrapolated merging temperature of the 5α-cholestan-3β-yl series is about 10° lower than that of the cholesteryl series. The two branches of the cholesteric–isotropic transition temperatures of S-cholesteryl ω-phenylalkanethioates are spread farther apart and the odd–even effect might persist to a much higher homologue than the 20th member. However, the temperature region at which the two branches might merge can be expected in the vicinity of that of the corresponding series of cholesteryl ω-phenylalkanoates.

The data obtained are not sufficient to explain the observed odd–even effect. Nevertheless, a few parameters can be pointed out which may be responsible for this unusual effect. A terminal phenyl group in the 3β-acyl moiety causes a differentiation of mesomorphic properties, which decreases with increasing chain length. Since the extension of the ester chain by a methylene group does not appreciably change polarizability and size of the molecule, two distinct configurations of the molecule in the mesophase must be assumed, one for even and one for odd chain length. Dreiding stereo models (Fig. 4) display a difference for odd and even members in the relative position of the phenyl group with respect to the carbonyl group.

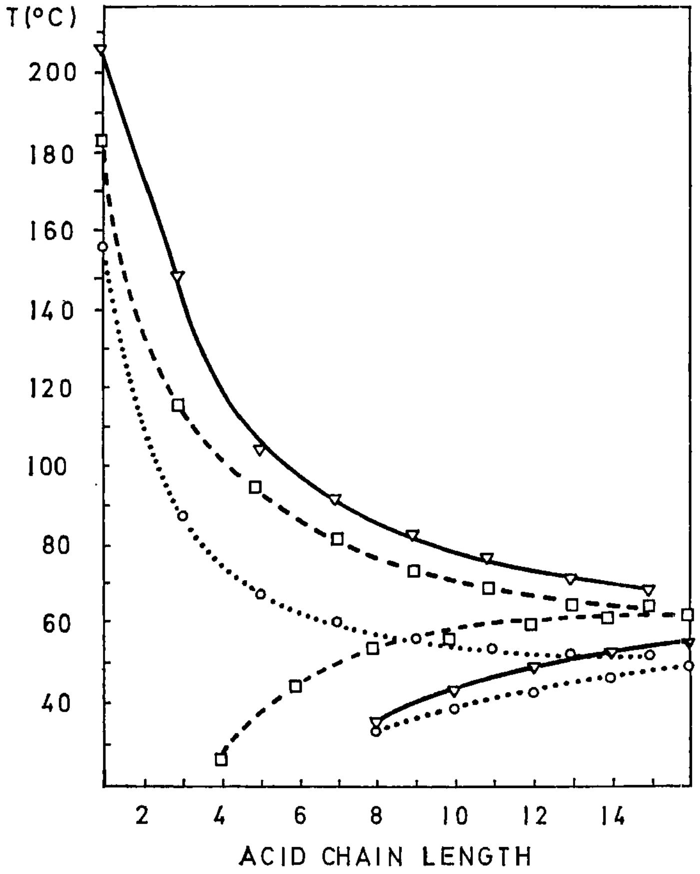


Figure 3. Cholesteric–isotropic phase transitions. - - □ - - , cholesteryl ω-phenylalkanoates; ·· ○ ·· , 5α-cholestan-3β-yl ω-phenylalkanoates; —▽—, S-cholesteryl ω-phenylalkanethioates.

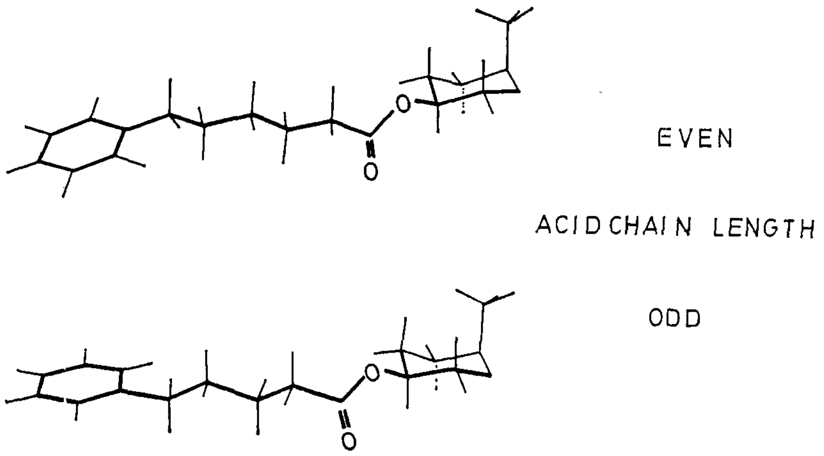


Figure 4. Dreiding stereo models depicting an even and an odd ω-phenylalkanoate.

We notice a *cisoid* arrangement for even and a *transoid* arrangement for odd ω-phenylalkanoates. The resulting difference in side spacing might explain the alternations of phase transition temperatures between members of odd and even chain length. Since the flexibility of the acyl chain becomes greater with increasing chain length, the alternations should become smaller and this, indeed, is observed. If our assumption is correct, this odd–even effect of phase transitions should also be observed with bulky terminal groups other than the phenyl group in the ester chain.

Acknowledgements

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