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Mesomorphism of Homologous Series. II. Odd-Even Effect†

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Abstract—The determination of mesomorphic behavior was extended to cover the first sixteen members of the cholesteryl ω-phenylalkanoates. Microscopy and scanning calorimetry were used to identify the mesophases and to measure transition temperatures and associated latent heats. The clearing temperatures fall on two distinct curves: a high temperature branch occurring for odd numbers of C-atoms of the acid chain and a low temperature branch occurring for even numbers of C-atoms. The difference in clearing points of neighboring homologues decreases from about 100 °C for low members to a few degrees for high members of the series. Contrary to this, the smectic-cholesteric transition temperatures show no such odd-even effect, although their enthalpies and entropies do exhibit a pronounced odd-even behavior. The enthalpies and entropies of the cholesteric-isotropic transitions show an odd-even effect where the odd chain length branch has the high values, whereas for the smectic-cholesteric transitions the even chain length branch has the high values. The entropies of clearing are reduced for even but increased for odd chain length, when compared with corresponding members of the cholesteryl alkanoate series. An attempt is made to determine the reason for this unusual behavior.

Introduction

The cholesteryl ω-phenylalkanoates exhibit a very unusual effect. The cholesteric-isotropic transition temperatures (Ch–I temperatures) alternate with the acid chain length by an amount which gradually decreases with increasing chain length. This unusual type of dependence—briefly called the odd-even effect—was established previously for the first eight members of the series.⁽¹⁾‡ It is the

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‡ Gray, G. W. and Harrison, K. J. (2) discussed an unusually large odd-even alternation of the *nematic* clearing temperatures for ω-phenylalkanoates of 4-*p*-substituted benzylideneaminocinnamic acids. Unfortunately these results cannot be related to ours, because of the lack of information on the molecular arrangement in cholesteric mesophases.

purpose of this work to extend the study of this odd-even effect to higher homologues and to determine whether the smectic-cholesteric transition temperatures (S–Ch temperatures) exhibit an odd-even effect. Furthermore, an attempt is made to correlate the alternation of the Ch–I transition temperatures with certain molecular properties.

Experimental Results

The cholesteryl ω-phenylalkanoates were prepared⁽³⁾ employing Staab's esterification method. Thin layer and gas-liquid chromatographic tests of the starting materials and of the final product indicate a purity of 99% or better. We determined the transition temperatures and transition heats with a modified differential scanning calorimeter and identified the mesomorphic phases under the microscope with a temperature programmed stage.†⁽⁴⁾ The temperature measurements of both the scanning calorimeter and the programmed microscope stage agreed within the limit of error.⁽⁵⁾ We found that except for the cholesteryl phenylacetate all compounds exhibit a cholesteric mesophase and in addition a smectic mesophase for the 8-phenyloctanoate, 10-phenyldecanoate and subsequent members. The transition temperatures and entropies are compiled in Table 1.

In Fig. 1 we plotted the transition temperatures versus the chain length, using the previously reported data for the first eight members of the series. The melting curve exhibits the customary erratic behavior indicating the existence of frozen-in non-equilibrium states and of possible low temperature crystal modifications. The latter may also explain the fact that we obtained two melting points for many of the compounds, a low and a high one, depending on the thermal history. The low temperature limit of the mesomorphic state is indicated by the onset of freezing obtained at a cooling rate of 10 °C per minute. Note that most compounds are monotropic and that the low temperature mesophases could be observed only because of extreme undercooling of the melt. The S–Ch transition temperatures do not exhibit an odd-even effect but increase linearly with chain length. The latter is remarkable, as such an unexpected linear relationship has not been reported. The clearing points fall

† Microscope furnace FP–2, Mettler Corporation.

TABLE 1 Cholesteryl ω-Phenylalkanoates

Temperatures, Enthalpies and Entropies of Transition

n + 1	T_{MP} °C	H_{MP} K cal/mol	S_{MP} cal/mol K	T_{S-Ch} °C	H_{S-Ch} K cal/mol	S_{S-Ch} cal/mol K	T_{Ch-I} °C	H_{Ch-I} K cal/mol	S_{Ch-I} cal/mol K
1	150.5	7.82	18.5	—	—	—	182.6	0.16	0.35
2	120.5	6.85	17.4	—	—	—	—	—	—
3	111.5	8.77	23.2	—	—	—	114.1	0.12	0.32
4	90.9	6.74	18.5	—	—	—	26.1	0.02	0.07
5	98.3	7.50	20.2	—	—	—	91.3	0.15	0.42
6	81.3	6.63	18.7	—	—	—	45.2	0.07	0.21
7	97.4	9.46	25.5	—	—	—	82.7	0.19	0.53
8	91.2	9.17	25.0	34.7	0.14	0.47	56.6	0.084	0.26
9	108.0	10.41	27.3	—	—	—	73.4	0.19	0.55
10	74.3	8.78	25.3	35.9	0.12	0.39	55.0	0.082	0.25
11	81.2	9.05	25.5	—	—	—	69.8	0.22	0.64
12	68.4	9.32	27.3	44.0	0.17	0.54	59.9	0.15	0.45
13	72.6	10.72	31.0	46.6	0.11	0.34	65.6	0.34	1.00
14	63.4	10.16	30.2	48.4	0.27	0.84	61.2	0.19	0.57
15	73.1	11.87	34.3	51.1	0.18	0.56	66.3	0.42	1.24
16	53.1	13.90	42.6	51.3	0.28	0.86	61.9	0.23	0.69

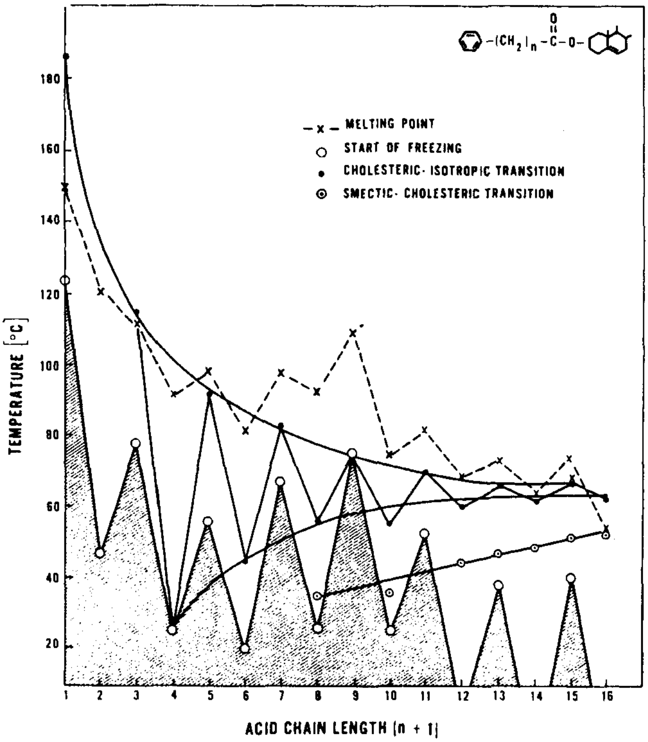

Figure 1. Transition temperatures of the cholesteryl ω-phenylalkanoates.

on two distinct branches: the high temperature branch for odd and the low temperature branch for even chain length. As predicted[(4)] the two branches approach each other with increasing chain length. The new data indicate that the odd-even effect may not exist beyond the eicosanoate.

Figure 2 shows a close hyperbolic curve fit to the branches. The difference between the measured temperature T_m and the calculated temperature T_c amounts to less than ± 2 °C for the odd and to less than ± 3 °C for the even branch. Considering the ± 0.4 °C uncertainty of the temperature measurements and the probably much stronger influence of impurities on the clearing points, the curve fit is excellent. The fact that the first eight compounds of the homologous series were prepared and their data measured about two years earlier speaks well for the reliability of the chemical preparation and for the reproducibility of the temperature measurements. Even a

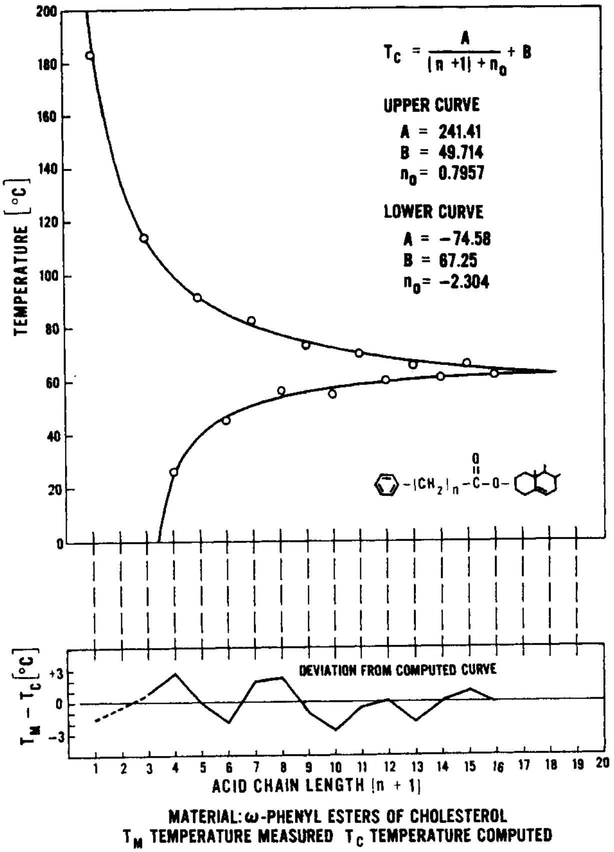

Figure 2. Curve fitting of cholesteric-isotropic transitions.

crude inspection of the ten homologous series(2,5,6) investigated by our group shows that this result is the best fit for any of the series.

The enthalpies and entropies of fusion, displayed in Fig. 3, exhibit the usual erratic dependence on chain length. As already reported for other homologous series,(2,5) this is not surprising, because we did not attempt to bring the crystalline state into thermal equilibrium. A definite chain length dependence of temperatures, enthalpies and entropies of fusion can be expected only if the solid phase is in thermal equilibrium and if its structure depends on the chain length in a regular manner. Since mesophases equilibrate faster and may have the same type of molecular arrangement for the same class of mesophase, the transitions in the melt exhibit smooth relations for transition temperatures and—to a lesser degree because of the large uncertainty of the measurements—for the associated enthalpies and entropies.

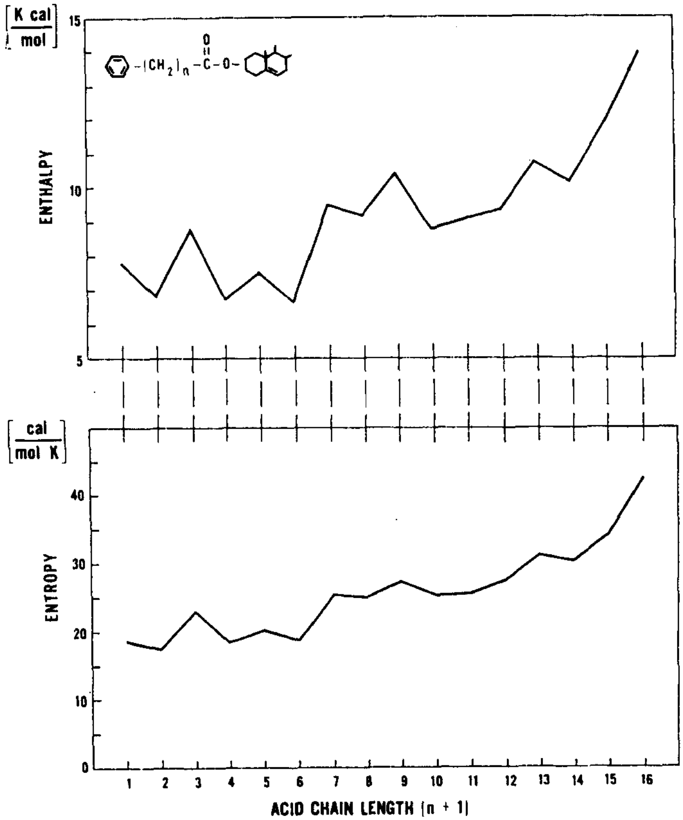

Figure 3. Enthalpies and entropies of fusion.

Figure 4 shows the enthalpies and entropies of the S–Ch transitions. It is surprising that these quantities exhibit a strong odd-even effect, because the associated transition temperatures depend linearly on chain length! As expected, the enthalpies and entropies of the Ch–I transitions (see Fig. 5) show an odd-even effect in which the branch for odd chain length carries the high values. The latter is the same

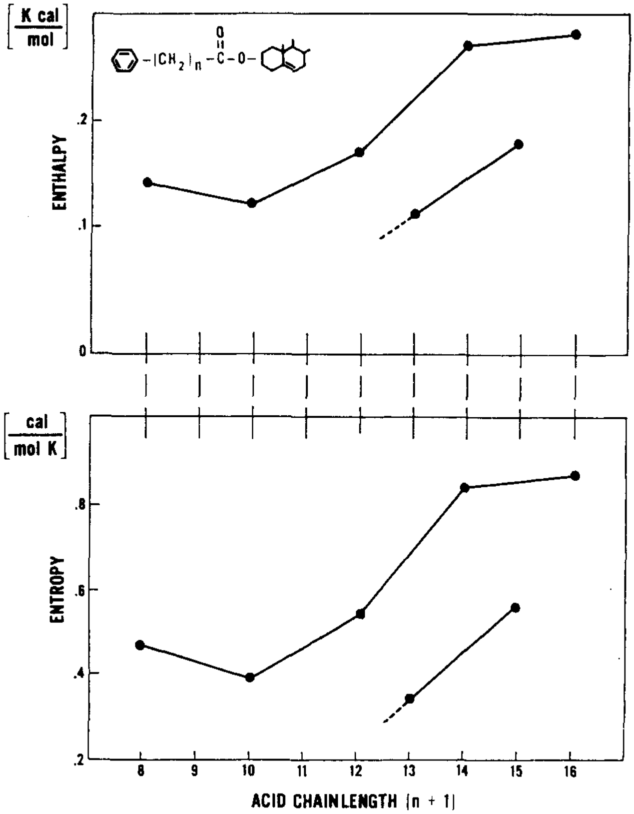

Figure 4. Enthalpies and entropies of smectic-cholesteric transitions.

for the clearing temperatures but opposite to the odd-even effect of the enthalpies and entropies of the S–Ch transitions.

Discussion

To interpret these results we first compare the mesomorphic behavior of the cholesteryl ω-phenylalkanoates with that of the corresponding cholesteryl alkanoates and then discuss the variations of the mesomorphic properties within the ω-phenyl series. We will attempt to infer from these considerations molecular features which may be responsible for the odd-even effect.

Table 2 shows that the replacement of a methyl hydrogen of the

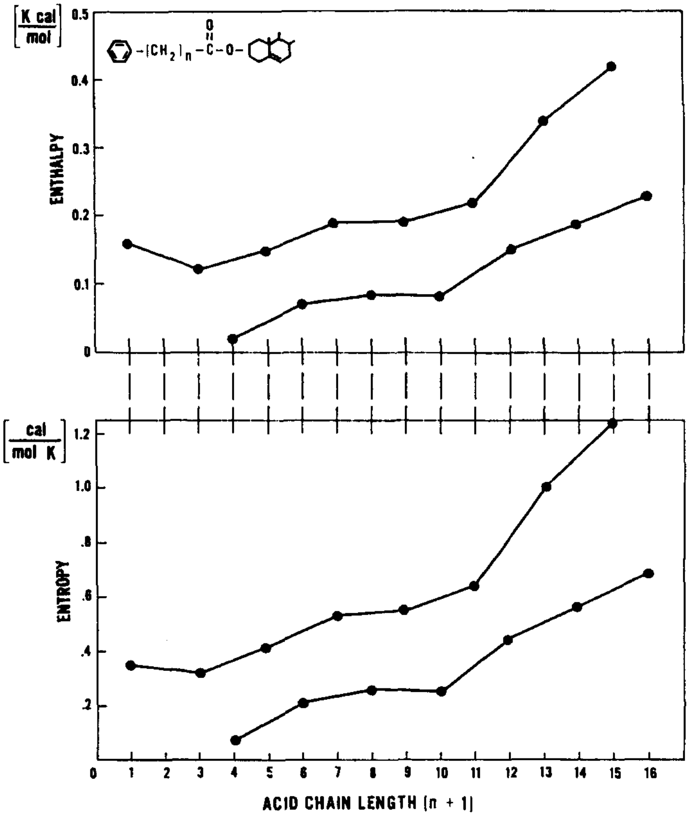

Figure 5. Enthalpies and entropies of cholesteric-isotropic transitions.

cholesteryl alkanoates by a phenyl group results in the following changes:

1. All Ch–I transition temperatures are substantially lowered, except for the benzoate† and the phenylpropionate.
2. All S–Ch transition temperatures and associated entropy changes are decreased.
3. For corresponding homologues the temperature difference between the Ch–I and the S–Ch transitions is increased by 6 to 13 °C (increased temperature range of the cholesteric mesophase!).

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† The unusually low Ch–I transition temperature of cholesteryl formate may be caused by a preferred conformation in which the formyl hydrogen atom stays close to the 3α-hydrogen.(8)

TABLE 2 Comparison of the Mesomorphic behavior of the Alkanoates and ω-Phenylalkanoates of Cholesterol

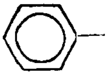
Transition Temperature and Entropy Differences between corresponding Homologues

n + 1	$T_{S-Ch} - T_{S-Ch}^{\omega}$ °C	$S_{S-Ch} - S_{S-Ch}^{\omega}$ cal/mol K	$T_{Ch-I} - T_{Ch-I}^{\omega}$ °C	$S_{Ch-I} - S_{Ch-I}^{\omega}$ cal/mol K	A = $T_{Ch-I} - T_{S-Ch}$ °C	B = $T_{Ch-I}^{\omega} - T_{S-Ch}^{\omega}$ °C	B − A °C
1	—	—	−122.2	−0.07	—	—	—
2	—	—	—	—	—	—	—
3	—	—	0.0	−0.02	—	—	—
4	—	—	85.7	0.22	—	—	—
5	—	—	18.0	−0.13	—	—	—
6	—	—	55.2	0.14	—	—	—
7	—	—	10.0	−0.20	—	—	—
8	—	—	38.1	0.17	—	—	—
9	—	—	18.7	−0.10	—	—	—
10	43.1	0.04	35.9	0.25	11.9	19.1	7.2
11	—	—	20.2	0.03	—	—	—
12	38.1	0.29	29.3	0.26	8.1	15.9	7.8
13	32.2	0.44	19.2	−0.28	6.0	19.0	13.0
14	31.5	0.03	24.0	0.13	5.3	12.8	7.5
15	27.2	0.54	16.6	−0.51	4.6	15.2	10.6
16	26.8	0.24	20.7	0.14	4.5	10.6	6.1

Note: Superscript ω refers to ω-phenylalkanoates. Absence of superscript refers to alkanoates.

4. The entropies of clearing are reduced for even but increased for odd acid chain length, except for an experimental deviation for the undecanoate.

Obviously these changes are caused by the larger dimensions, the higher polarizability and the greater anisotropy of the phenyl ring:

Dimensions:	H	~1 Å	diameter
		≈ 5 Å	diameter, ≈ 2.5 Å thickness
Polarizability:	H—C	0.79 Å^3	parallel to bond
		0.58 Å^3	perpendicular to bond
	—C	≈ 12 Å^3	parallel to plane†
		≈ 6 Å^3	perpendicular to plane†

The decrease of the S–Ch transition temperatures and of the associated entropy changes may be explained by the increase of the lateral spacing of the molecules due to the bulkiness of the phenyl ring. Apparently the 10 to 20 times higher polarizability of the latter is not sufficient to overcome the resulting weakening of the lateral attractions, because the intermolecular forces (van der Waal's forces) are inversely proportional to the sixth power of the molecular distance. This may also be the reason for the lowering of the clearing points. However, this argument does not carry the same weight as the previous one, because we cannot explain the cholesteric behavior in terms of lateral and terminal attractions between molecules. The greater complexity of the molecular interaction is also indicated by the fact that the S–Ch transition temperatures are more depressed than the Ch–I transition temperatures and that the clearing entropies are increased for odd, but decreased for even chain length.

Next we compare the mesomorphic behavior between odd and even members of the ω-phenyl series. We observed (a) an extremely large odd-even effect of the Ch–I transition temperatures and of the

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† Hirschfelder *et al.*⁽⁷⁾ list 12.3 and 6.3Å^3 for the polarizability of the benzene ring. The replacement of a C–H bond by a C–C bond varies the polarizabilities, depending upon the C–C orientation, by an amount insignificant for our qualitative considerations.

associated entropy changes, (b) no odd-even effect for S–Ch transition temperatures, and (c) a pronounced odd-even effect of the S–Ch transition entropies.

Since the extension of the acid chain by a methylene group does *not* appreciably change the polarizability and size of the molecule, the odd-even effect must be caused by two distinct molecular conformations—one for odd and another for even chain lengths. Considering that molecular parallelism is an essential condition for the existence of nematic structures in general and thus for " twisted nematic structures " (i.e. for certain cholesteric mesophases) in particular, we assume a stretched out molecular conformation. Fig. 6 shows that the direction of the bond linking the phenyl ring with the acid chain is in a cis-like configuration with respect to the carbonyl group for even and in a trans-like configuration for odd chain length. As the chain length increases, small random deviations of the carbon atoms of the zig-zag configuration gradually diminish the distinction between the two configurations. This may explain the decrease of the odd-even effect with chain length. Of course the same conformations should exist for the corresponding cholesteryl alkanoates. But the difference between the two series must be due to the fact that the phenyl ring is bulkier, more polarizable and anisotropic than the terminal hydrogen. Consequently the angular variations of the phenyl ring orientation should have a more pronounced effect on the mesomorphic state.

We know that the substitution of sulfur for the 3β-oxygen strongly increases the temperatures of mesomorphic transitions.(2,6c) This indicates the critical importance of the molecular interaction between

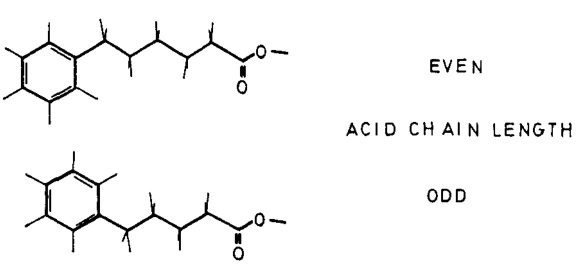

Figure 6. Configuration of odd and even cholesteryl ω-phenylalkanoates. (Depicted by 6-phenylhexanoate and 5-phenylpentanoate)

the carbonyl group and the neighboring molecules. Therefore it should be significant as to whether the strongly polarizable phenyl ring supports or counteracts the effect of the carbonyl group on neighboring molecules. However, direction and magnitude of the molecular interactions at the phenyl ring and at the carbonyl group depend on their degree of freedom and on the respective local electric fields. As long as insufficient information on these factors exists we cannot find a conclusive explanation of the odd-even effect. We can only hope that it is meaningful to correlate odd and even conformations with the odd-even effect.

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