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Cholesteryl ω-Phenylalkanoates

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Abstract—A homologous series of cholesteryl ω-phenylalkanoates was synthesized from cholesterol and the imidazolides of ω-phenylalkanoic acids. The mesomorphic properties of 16 members, cholesteryl benzoate through cholesteryl 16-phenylhexadecanoate, were determined microscopically. All homologues, except cholesteryl phenylacetate, show a cholesteric mesophase. A monotropic smectic mesophase is found in cholesteryl 8-phenyloctanoate, 10-phenyldecanoate and higher members. The values of the cholesteric–isotropic transition temperatures alternate with increasing chain length, but the smectic–cholesteric transition temperatures do not show this odd–even effect. Cholesteric colors are exhibited by most of the cholesteryl ω-phenylalkanoates and a well-defined visible spectrum of selectively reflected light by cholesteryl 10-phenyldecanoate and successive homologues.

The most intensively studied cholesteric compounds are the readily available cholesteryl alkanoates. Their clearing point curve[1] has a maximum temperature at cholesteryl propionate and thereafter decreases steadily with increasing chain length. The deviations of the cholesteric–isotropic transition points from an idealized curve are very small and therefore in accordance with Gray's observation concerning purity and a smooth curve relationship within a homologous series.[2] The cholesteric–isotropic transition temperatures of S-cholesteryl alkanethioates,[3] however, show a small but distinct alternation between odd and even members for the first ten homologues and thereafter a monotonic decrease with chain length. Impurities cannot account for this alternation, because the same alkanoic acids were used in the preparation of both homologous series.

A pronounced alternation of the clearing points was observed throughout the homologous series of cholesteryl ω-phenylalkanoates.[4] The cholesteric–isotropic transition temperatures fall on two

distinct curves: a high temperature branch for odd and a low temperature branch for even members. The difference in cholesteric–isotropic transition temperatures between neighboring homologues decreases from about 100° for low members to a few degrees for high members of the series. The smectic–cholesteric transitions, however, do not show this odd–even effect. This remarkable effect of an ω-phenyl group on the clearing points is not restricted to the isotropic–cholesteric transition. It was found in S-cholesteryl ω-phenylalkanethioates for smectic–cholesteric transitions[5] and in p-substituted ω-phenylalkyl (benzylideneamino) cinnamates for nematic–isotropic transitions.[6]

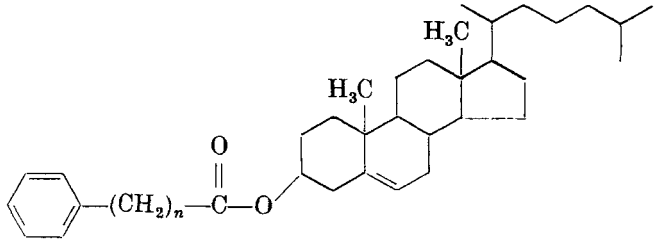
It is interesting to compare these observations with the melting point curve of ω-phenylalkanoic acids.[7,8] The melting temperatures pass through a minimum at 7-phenylheptanoic acid and then increase with chain length. An alternating effect is exhibited by 11-phenylundecanoic and higher acids, with the even acids having higher melting points. In contrast, the even ω-phenylalkanoates of cholesterol,[4] 3β-mercaptocholest-5-ene,[5] and 5α-cholestan-3β-ol[5] form the low temperature branches of the cholesteric–isotropic transition curves. With Dreiding stereo models one can easily demonstrate a *cisoid* conformation of the phenyl group with respect to the extended (zigzag) methylene chain for even and a *transoid* conformation for odd ω-phenylalkanoates.[4,5] The resulting difference in side spacing, and a greater anisotropy and polarizability of the phenyl ring as compared with a terminal methyl group,[4] may be responsible for these unusual effects.

This paper will mainly discuss the preparation of cholesteryl ω-phenylalkanoates, and their precursors, and will describe optical investigations made with its cholesteric members, because the thermodynamic data of this homologous series have already been published.[4]

1. Preparation

The reaction of the imidazolides of ω-phenyalkanoic acids with cholesterol under catalysis with sodium methoxide[9] was found to be the most feasible of several esterification methods[3] investigated. Yields of analytically pure compounds ranged from 60–70%, but

were only about 30–40% without the addition of sodium methoxide.



I

The historically famous cholesteryl benzoate[10] and the next four homologues[11,12,13] had already been reported. We reinvestigated these compounds and extended the series to cholesteryl 16-phenylhexadecanoate. The crude compounds, which contained minute amounts of cholesta-3,5-diene and unreacted cholesterol, were purified by column chromatography on silica gel using mixtures of *n*-hexane and benzene as eluent, and then recrystallized from ethanol. Thin-layer chromatography was used to monitor the reaction and the purification. The physical properties of the synthesized cholesteryl ω-phenylalkanoates (I) and their elemental analyses[14] are summarized in Table 1. The yields are expressed in analytically pure materials, *i.e.*, after chromatography and recrystallization. Transition points were determined microscopically with a Mettler FP 2 hot stage, and the temperature readings are corrected.

In Fig. 1 the transition temperatures of cholesteryl ω-phenylalkanoates are plotted *versus* the chain length. The melting points show an irregular behavior. The cholesteric–isotropic transition temperatures alternate regularly with chain length and form two curves which can be mathematically expressed as hyperbolas[4]: the high temperature curve for odd, and the low temperature curve for even members. Cholesteryl 8-phenyloctanoate, 10-phenyldecanoate, and successive members also form a monotropic smectic mesophase, but the smectic–cholesteric transition temperatures increase almost linearly with chain length. Cholesteric colors, exhibited by most members of this series, will be discussed in detail in Sec. 2.

TABLE 1 Cholesteryl ω-phenylalkanoates

ω-phenylalkanoate	Yield (%)	Transition temperatures mp	S–Ch[a]	Ch–I[b]	Formula	Mol. wt.	Analytical values, (%) Calculated C	H	O	Found C	H	O
benzoate	68	149.5[c]	—	178.7[c]	—	—	—	—	—	—	—	—
phenylacetate	68	122.5[d]	—	—	—	—	—	—	—	—	—	—
3-phenylpropionate	65	114.0[e]	—	114.6[e]	—	—	—	—	—	—	—	—
4-phenylbutyrate	62	90.6[f]	—	26.2[f]	$C_{37}H_{56}O_2$	532.9	83.40	10.59	6.01	83.54	10.73	6.26
5-phenylpentanoate	65	100.0[g]	—	91.0[g]	$C_{38}H_{58}O_2$	546.9	83.46	10.69	5.85	83.35	10.66	5.89
6-phenylhexanoate	63	82.0	—	44.3	$C_{39}H_{60}O_2$	560.9	83.51	10.78	5.70	83.42	10.78	5.84
7-phenylheptanoate	64	96.2	—	83.2	$C_{40}H_{62}O_2$	574.9	83.56	10.87	5.57	83.33	10.98	5.67
8-phenyloctanoate	61	92.0	34.7	56.4	$C_{41}H_{64}O_2$	589.0	83.61	10.95	5.43	83.89	11.09	5.46
9-phenylnonanoate	60	110.0	—[h]	76.6	$C_{42}H_{66}O_2$	603.0	83.66	11.03	5.32	83.71	11.07	5.35
10-phenyldecanoate	70	77.2	39.2	56.4	$C_{43}H_{68}O_2$	617.0	83.71	11.11	5.19	83.61	11.15	5.14
11-phenylundecanoate	67	82.7	43.7[i]	71.6	$C_{44}H_{70}O_2$	631.1	83.75	11.18	5.07	83.68	11.28	5.21
12-phenyldodecanoate	63	68.0	43.3	58.3	$C_{45}H_{72}O_2$	645.1	83.79	11.25	4.96	83.84	11.06	4.86
13-phenyltridecanoate	70	74.9	47.5	68.4	$C_{46}H_{74}O_2$	659.1	83.83	11.32	4.86	83.85	11.46	4.93
14-phenyltetradecanoate	69	64.1	48.5	60.3	$C_{47}H_{76}O_2$	673.1	83.86	11.38	4.75	83.92	11.47	4.83
15-phenylpentadecanoate	68	74.0	51.3	66.8	$C_{48}H_{78}O_2$	687.2	83.90	11.44	4.66	83.80	11.32	4.56
16-phenylhexadecanoate	65	55.0	51.2	61.4	$C_{49}H_{80}O_2$	701.2	83.94	11.50	4.56	83.86	11.52	4.46

(a) Smectic–cholesteric transition, °C; (b) cholesteric–isotropic transition, °C; (c) reported[10] mp 149–150°; cp 178°; (d) reported[11] mp 118°; (e) reported[12] mp 106°; cp 110°; (f) reported[13] mp 89.2; cp —; (g) reported[13] mp 94.8; cp 90.0°; (h) sample crystallizes at 56.5°; (i) not obtainable by DSC because of crystallization.[4]

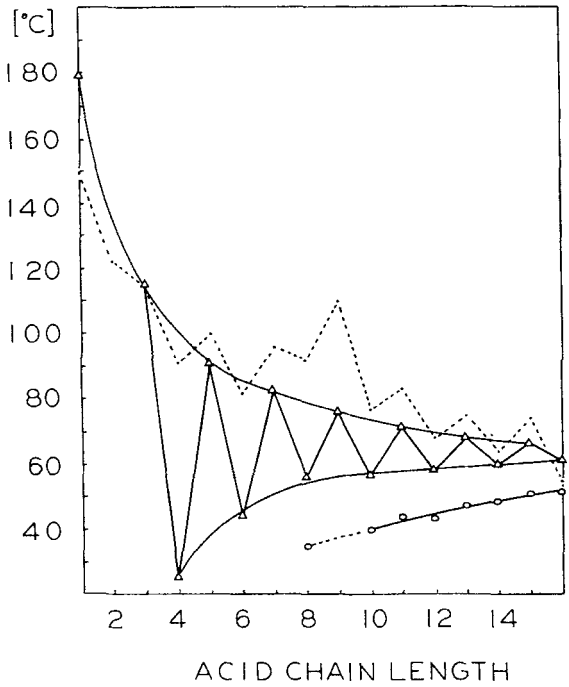


Figure 1. Transition temperatures of cholesteryl ω-phenylalkanoates: ----, melting points; —△—, cholesteric–isotropic transitions; —○—, smectic–cholesteric transitions.

2. Experimental Part

I. Starting Materials

(a) *Cholesterol*—Commercial cholesterol, which we purified by the bromination–debromination method of Fieser,[15] was found to be uniform on two-dimensional thin-layer chromatography.[16]

(b) *ω-Phenylalkanoic acids*—The lower members were purchased: benzoic acid and phenylacetic acid from Columbia Organics, Columbia, SC (Fluka); 3-phenylpropionic, 4-phenylbutyric, and 5-phenylpentanoic acids from Aldrich Chem. Co., Milwaukee, WI; and 6-phenylhexanoic acid from Sapon Laboratories, Oceanside, NY. Depending on the availability of starting materials, we prepared the higher members by chain elongation *via* enamines[17] or *via* organocadmium ketone synthesis,[18] in either case followed by

Wolff-Kishner reduction of the intermediate keto ester. 7-Phenylheptanoic acid, bp 145–146°/2 Torr (rep.[7] bp 157–158°/2.5 Torr) and 8-phenyloctanoic acid, bp 148–150°/3 Torr (rep.[7] bp 205–208°/13 Torr) were prepared in analogy to Hünig *et al.*[17] 9-Phenylnonanoic acid was prepared according to Hase and Ohura,[7] mp 29–30° (rep. 29–30°). 10-Phenyldecanoic acid was synthesized in analogy to reported acylations[17] from 1-morpholino-1-cyclohexene and 4-phenylbutyryl chloride, mp 45.5–46.5° (rep.[7] 43.5–44.0°). 11-Phenylundecanoic acid, mp 45–46° (rep.[7] 43–44°), 12-phenyldodecanoic acid, mp 61–62° (rep.[19] 60.5–62°), and 13-phenyltridecanoic acid, mp 54.5–55.5° (rep.[8] 52–53°) were prepared *via* their dialkylcadmium derivatives according to published procedures. 14-Phenyltetradecanoic acid was synthesized from di(2-phenylethyl)cadmium and 11-carbomethoxyundecanoyl chloride, mp 70–71° (rep.[7] 68–69°). 15-Phenylpentadecanoic acid was synthesized from di(3-phenylpropyl)cadmium and 11-carbomethoxyundecanoyl chloride, mp 61.5–62.5°, and 16-phenylhexadecanoic acid was prepared according to literature, mp 74.5–75.5° (rep.[7] 73.5–74.5). All the acids used were distilled or recrystallized until gas chromatographic analysis of their respective methyl esters[20] on 15% EGSS-X and XE-61 (6-ft glass columns, silanized support) showed a minimum purity of 99%.

10-PHENYLDECANOIC ACID — A solution of 83.5 g (0.46 mol) of 4-phenylbutyryl chloride in 100 ml of chloroform was added within 1 hr to a stirred solution of 84.1 g (0.5 mol) of 1-morpholino-1-cyclohexene[21] and 55.5 g (0.59 mol) of triethylamine in 200 ml of dry chloroform. After stirring for another 4 hr, 145 ml of 20% aq. HCl was added dropwise within 1 hr and then the mixture was boiled under reflux for 5 hr. The aqueous layer was separated and worked up. The residue, crude 2-(4′-phenylbutyryl)cyclohexanone, was reduced as reported for similar 2-acylcyclohexanones.[17] The crude acid was recrystallized from *n*-hexane and aqueous methanol. Yield 31.2 g (27.4%); mp 45.5–46.5°.

15-PHENYLPENTADECANOIC ACID — Di(3-phenylpropyl)cadmium was prepared by reacting a Grignard solution from 59.8 g (0.3 mol) of 1-bromo-3-phenylpropane and 7.65 g (0.315 g-atom) of magnesium

in 200 ml of anhydrous diethyl ether with 33.0 g (0.18 mol) of anhydrous cadmium chloride, followed by evaporation of the solvent and dissolution of the residue in 200 ml of absolute benzene. While stirred at room temperature, a solution of 11-carbomethoxyundecanoyl chloride,[22] prepared from 61.0 g (0.25 mol) of methyl hydrogen dodecanedioate[23] and 45 ml of freshly distilled thionyl chloride, in 100 ml of absolute benzene was added dropwise within 30 min. The mixture was then heated under reflux for 2 hr, cooled, and decomposed by addition of 10 ml of H_2O and 100 ml of 2N H_2SO_4. The organic layer was washed successively with H_2O, 10% aq. Na_2CO_3, H_2O, and dried. After evaporation of the solvent, the residue was distilled *in vacuo* and yielded 58.0 g (68%) of a colorless liquid (bp 216–217°/1 Torr) which crystallized on standing. The analytical sample of *methyl 12-keto-15-phenylpentadecanoate* was obtained by recrystallization from *n*-hexane: mp 45–46.5°.

Calc'd for $C_{22}H_{34}O_3$ (346.5): C, 76.26; H, 9.89; O, 13.85.

Found: C, 76.28; H, 9.98; O, 13.96.

A small sample was hydrolyzed with dilute NaOH, and the isolated *12-keto-15-phenylpentadecanoic acid* recrystallized from aqueous ethanol: mp 69.5–71°.

Calc'd for $C_{21}H_{32}O_3$ (332.5): C, 75.86; H, 9.70; O, 14.44.

Found: C, 75.72; H, 9.84; O, 14.34.

54.0 g of the preceding keto ester, 35 ml of hydrazinium hydroxide, and 50 g of KOH in 200 ml of 2,2′-oxydiethanol were heated to about 150° until all volatile matter had distilled off. Then the temperature was gradually increased and held at 200° overnight. After cooling, the reaction mixture was diluted with H_2O, acidified with 85 ml of conc. aq. HCl, and the precipitated acid extracted into chloroform. After the usual work-up, the crude acid was recrystallized twice from *n*-hexane/ethanol (95/5). Yield 36.5 g (73%), mp 61.5–62.5°.

Calc'd for $C_{21}H_{34}O_2$ (318.5): C, 79.19; H, 10.76; O, 10.05.

Found: C, 79.11; H, 10.57; O, 10.13.

II. Preparation of Compounds

The general procedure is exemplified with the synthesis of cholesteryl 15-phenylpentadecanoate. The proportions of reactants and solvent were the same in all synthetic procedures. The reactions were carried out in a nitrogen atmosphere.

CHOLESTERYL 15-PHENYLPENTADECANOATE — To a stirred slurry of 1.78 g (11 mmol) of 1,1′-carbonyldiimidazole in 50 ml of absolute benzene 3.18 g (10 mmol) of 15-phenylpentadecanoic acid was added, which dissolved almost completely with the evolution of CO_2. The last traces were dissolved by gentle warming. After cooling, a solution of 3.18 g (10 mmol) of cholesterol in 25 ml of absolute benzene was added and the reaction mixture stirred at room temperature for 30 min, then under reflux for 4 hr, with small amounts of sodium methoxide added twice. The progress of the reaction was monitored by thin-layer chromatography. The solvent was evaporated and the residue triturated with benzene/*n*-hexane (1/9), imidazole being precipitated. After filtration, the residue was chromatographed on silica gel (45 × 350 mm column, 0.05–0.2 mm, Merck) using benzene/*n*-hexane (3/7) as eluent. The fractions containing the pure compound were combined, the solvent evaporated, and the residue recrystallized from ethanol. Yield: 4.7 g (68%); mp 74.0°.

III. Purity

Thin-layer chromatographic analysis of the crude reaction mixture revealed only two minor side products of the transacylation reaction, one of which could be identified as cholesta-3,5-diene. Another minor impurity was unreacted cholesterol. All three contaminants could be removed by column chromatography on silica gel. A thorough thin-layer chromatographic investigation in several solvent systems, in two dimensions, and on silver nitrate-impregnated layers, did not reveal any other detectable impurity. A gas chromatographic analysis of cholesteryl benzoate also did not result in the detection of other side products. Considering these analytical results and the purity of the starting materials used in these experiments, we can safely assume a purity of 99% or better in the synthesized cholesteryl ω-phenylalkanoates.

IV. Cholesteric Properties

Because surface forces may influence the formation of cholesteric textures, all samples were investigated between two clean glass cover slides. The cholesteric colors, observed in the lower members of this series, are usually covering a wide temperature range and are frequently obtained only on fast cooling or on mechanical disturbance

of the sample at the appropriate temperature. Therefore, the temperatures could not be corrected for thermal lag due to varying heating and cooling rates. These rates were chosen to facilitate observations rather than to obtain thermal equilibrium. But, in general, these observations are in close agreement (± 2°) with the data obtained by differential scanning calorimetry.[4] The visible spectrum of selectively reflected light, exhibited mainly by the higher members, could be determined accurately. Some of the members also exhibited " platelets " which we described extensively in the homologous series of cholesteryl *n*-alkyl carbonates.[24] The colors, except where noted, were observed on cooling the sample from the isotropic state, and were reversible with temperature in the melted state.

Cholesteryl benzoate, mp 149.5°, cp 178.7°. Its cholesteric behavior has been intensively investigated in the past.

Cholesteryl phenylacetate melts at 122.5° and freezes at 46.4°. It may not be mesomorphic because the extrapolation of the cholesteric–isotropic transition temperature curve (Fig. 1) indicates a clearing point lying about 50° below the freezing point.

Cholesteryl 3-phenylpropionate melts at 114.0° and forms the plane cholesteric texture which displays an intense green color. At 114.5° much dimmer green platelets form which disappear at 114.6°, the clearing point. On cooling from the isotropic state, the green platelets form at 114.6°, which change their color to yellow at 114.3°, to orange at 114.1°, to orange-red at 113.9°, and to red at 113.6°. At 113.2° the red platelets are replaced by focal-conic bands, which persist to about 70° where the material crystallizes.

Cholesteryl 4-phenylbutyrate melts at 90.6° and clears at 26.2° without displaying any colors on either heating or cooling, but showing the focal-conic texture typical of cholesteric mesophases.

Cholesteryl 5-phenylpentanoate, mp 100.0°, cp 91.0°, displays a blue color at 61.2°, which changes to green at 52.6° and to yellow at 39.2°, where crystallization starts.

Cholesteryl 6-phenylhexanoate melts at 82.0° and clears at 44.3°. The visible spectrum can be obtained briefly on mechanical disturbance at about 44°.

Cholesteryl 7-phenylheptanoate, mp 96.2°, cp 83.2°, displays violet, blue and green colors between 83° and 82° and crystallizes at 72°.

Cholesteryl 8-*phenyloctanoate*, mp 92.0°, cp 56.4°, displays the entire visible spectrum on fast cooling at about 35°.

Cholesteryl 9-*phenylnonanoate*, mp 110.0°, cp 76.6°, forms violet platelets at 76.6° on cooling. These change to green platelets at 76.5° and to yellow platelets at 76.4°. The plane texture (blue color) appears at 74.5° and recrystallization starts at 56.5°.

Cholesteryl 10-*phenyldecanoate*, mp 77.2°, cp 56.4°, exhibits the visible spectrum at 39.5–39.3° on cooling.

Cholesteryl 11-*phenylundecanoate* melts at 82.7°, cp 71.6°. On cooling, violet platelets appear at 71.6°, which change to blue at 71.5°, to green at 71.3° and to yellow at 70.6°. The focal-conic texture forms at 69°, and changes to a faint blue plane texture on squeezing. On further cooling, the visible spectrum is exhibited at 47.0–44.2°.

Cholesteryl 12-*phenyldodecanoate* melts at 68.0° and clears at 58.3°. On cooling, the visible spectrum is displayed at 44.6–44.3°.

Cholesteryl 13-*phenyltridecanoate*, mp 74.9°, cp 68.4°, forms violet platelets at 68.4° on cooling which are replaced by the focal-conic texture at 64–61°. The visible spectrum is exhibited at 50.0–48.1°.

Cholesteryl 14-*phenyltetradecanoate* melts at 64.1° and clears at 60.3°. On cooling and mechanical disturbance, the visible spectrum is displayed at 48.7–48.5°.

Cholesteryl 15-*phenylpentadecanoate*, mp 74.0°, cp 66.8°, forms violet platelets on cooling at 66.8° which change to green at 64.7° and to the focal-conic texture at 63°. Further cooling yields the visible spectrum at 53.0–52.0°.

Cholesteryl 16-*phenylhexadecanoate* melts at 55.0° and clears at 61.4°. On cooling, the visible spectrum is exhibited at 51.7–51.3°.

Previously we found an alternation in the enthalpies, entropies, and temperatures of the cholesteric–isotropic phase transitions in this series. The high values are associated with the odd, and the low values with the even homologues.[4] Although the odd–even effect of the cholesteric–isotropic phase transitions is more pronounced with the lower members, a useful correlation between chain length and the observation of cholesteric colors can only be obtained with the higher members. Cholesteryl 10-phenyldecanoate and successive homologues can be divided into two groups. The even members exhibit a

narrow visible spectrum (0.2–0.4°) and no other colors on cooling. The odd members exhibit platelets just below the cholesteric–isotropic transitions and a wider visible spectrum of selectively reflected light (1.1–2.3°) at lower temperatures.

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