LIQUID CRYSTALS I. SYNTHESIS AND INVESTIGATION OF CHOLESTERYL FLUOROBENZOATES

By

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Cholesteryl *ortho-* *meta-* and *para*-fluorobenzoates have been prepared. The temperatures, enthalpies and entropies of the phase transitions have been measured with the aid of differential scanning calorimetry. Optical examination of the compounds has proved that all derivatives are enantiotropic cholesteric liquid crystals.

Introduction

One of the first and foremost investigated compounds showing liquid crystalline properties is cholesteryl benzoate [1]. Substituted cholesteryl benzoates studied to date include the *ortho-*, *meta-* and *para*-substituted chloro, bromo, iodo, nitro, methyl and methoxy derivatives, and some other di- and tri-substituted compounds [2, 3].

It seems reasonable to complement these compounds with the synthesis of the cholesteryl fluorobenzoates and compare their liquid crystalline properties with the features of the other halogeno-derivatives.

Experimental

Preparation

Cholesteryl *ortho-*, *meta-* and *para*-fluorobenzoates were prepared by the reaction of the corresponding acid chloride and cholesterol in the presence of triethylamine. The crude products were crystallized from benzene-ethanol mixtures. The purities of the compounds were checked with thin-layer chromatography, IR spectroscopy and combustion analyses. The analytical data on the compounds prepared are shown in Table I.

Table I

Analytical Data on the Compounds

Compound	Formula	C %		H %	
		Found	Calc.	Found	Calc.
Ortho	$C_{34}H_{49}O_2F$	80.58	80.27	9.79	9.71
Meta	$C_{34}H_{49}O_2F$	79.88	80.27	9.66	9.71
Para	$C_{34}H_{49}O_2F$	80.41	80.27	9.65	9.71

Calorimetry

Measurements were made with a PERKIN—ELMER DSC—2 calorimeter, in a highly-purified nitrogen atmosphere. The thermal calibration of the instrument was made with bidistilled water and with an indium standard. The weight of the samples was altered in the range 3—5 mg, with ±0.001 mg accuracy. The heating and cooling rates were 10°/min and the sensitivity of the instrument was 5—10 mcal/sec. The temperatures of the phase transitions could be reproduced with an accuracy of ±0.4°. The calorimetric calibration was made with a known quantity of indium standard.

Optical examination

For the measurement of melting points and the determination of the textures of the mesophases, a PHMK (VEB Analytik, Dresden) hot-stage apparatus and an AMPLIVAL POL-U (Carl Zeiss, Jena) polarizing microscope (equipped with a hot stage) were applied.

Results and discussion

The thermograms of cholesteryl *ortho-*, *meta-* and *para*-fluorobenzoates are shown in Figs. 1, 2 and 3, respectively.

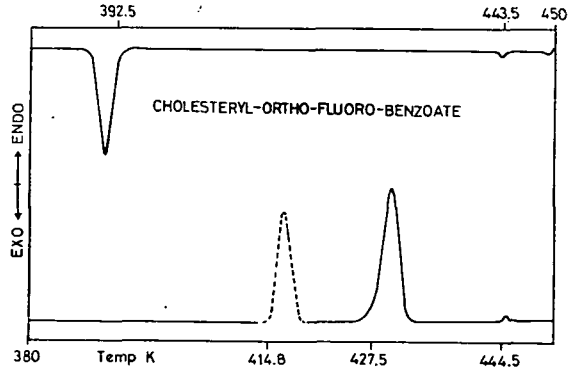

Fig. 1. Thermogram of cholesteryl *ortho*-fluorobenzoate

The lower parts of the diagrams show the phase transitions upon heating, and the upper regions of the diagram the phase transitions upon cooling. The full line means the first, and the dashed lines the second, *etc.* measurements in the heating mode (since differences may exist between the properties of solidified samples and those crystallized from solvents).

All three compounds show enantiotropic liquid crystalline phases. The thermal stabilities of the liquid crystalline states follow the sequence:

ortho < *meta* < *para.*

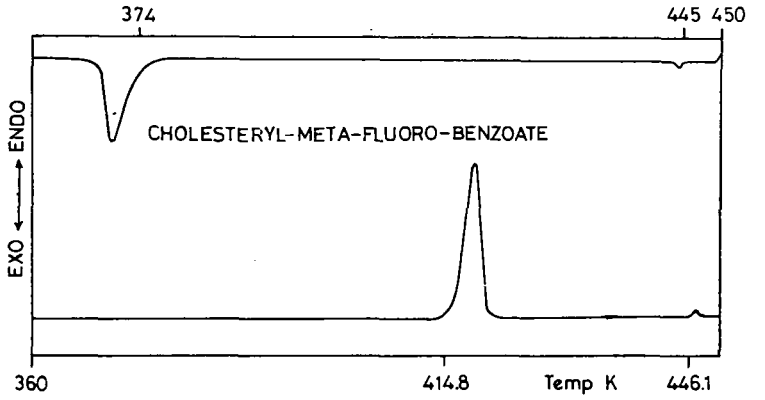

Fig. 2. Thermogram of cholesteryl *meta*-fluorobenzoate

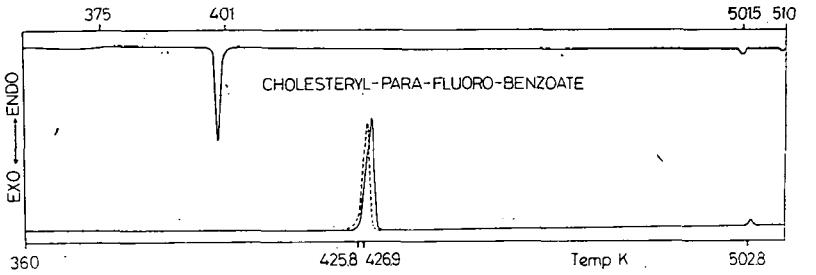

Fig. 3. Thermogram of cholesteryl *para*-fluorobenzoate

On the basis of the thermograms, the following phase transition schemes are characteristic for the changes in the state of the materials (Fig. 4).

Letter "C" means the crystalline state(s) of matter, symbol "Ch" represents the cholesteric mesophase, symbol "*I*" the isotropic liquid and symbol "*X*" the optically undetermined states.

Cholesteryl *ortho*-fluorobenzoate (Fig. 4, 2F) shows a simple enantiotropic cholesteric mesophase transition. The mesophase exists in a 31.3° temperature interval.

Cholesteryl *meta*-fluorobenzoate (Fig. 4, 3F) has two crystalline states. The "C_1" state comes from the crystallized sample, and the "C_2" state occurs when the sample is solidified from the isotropic melt. Thereafter, upon cooling and heating, only this latter state exists. Both states lead to an enantiotropic cholesteric state. This mesomorphic state is stable in a 31.5° temperature range.

Cholesteryl *para*-fluorobenzoate (Fig. 4, 4F) also has two crystalline states, but upon cooling after the cholesteric mesophase exists in an optically unobservable "X" state, and it follows the "C_2" crystalline state. The cholesteric mesophase is stable in a 77° interval.

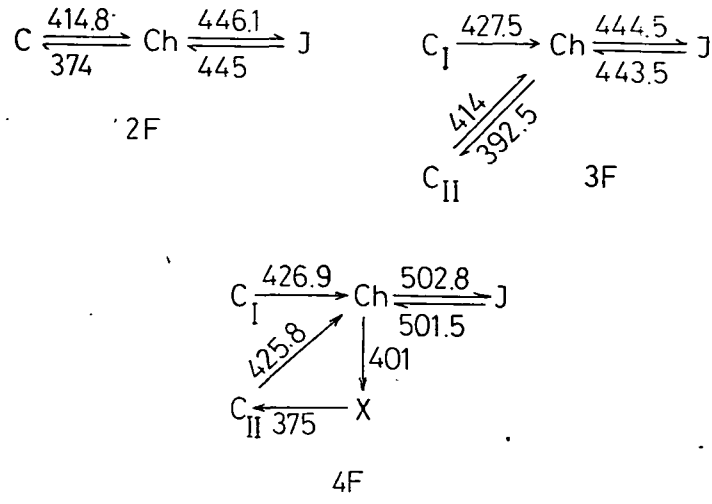

Fig. 4. Phase transition schemes of the compounds

The calorimetric values of the phase transitions were determined on the basis of the actual thermograms, because peak areas are proportional to the heat capacities of the phase transitions. The calculation was made with the following equation:

$$\Delta H = \frac{K \cdot A \cdot R}{W \cdot s}$$

Where ΔH = enthalpy change, R = sensitivity, K = instrument constant, W = weight of the sample, A = peak area, s = chart speed.

The peak areas were determined with a planimeter and also by weight measurement. The values of the enthalpy and entropy are shown in Table II.

Table II

Calorimetric Data on the Compounds

	ΔH (kcal/mol) C—Ch	ΔH (kcal/mol) Ch—I	Δs (kcal/mol K) C—Ch	Δs (kcal/mol K) Ch—I
Ortho	7.07*	0.13*	1.70×10^{-2}*	2.96×10^{-4}*
	5.83	0.13	1.40×10^{-2}	2.96×10^{-4}
Meta	9.78*	0.20*	2.29×10^{-2}*	4.46×10^{-4}*
	6.71	0.20	1.62×10^{-2}	4.46×10^{-4}
Para	7.72*	0.21*	1.81×10^{-2}*	4.25×10^{-4}*
	7.29	0.21	1.71×10^{-2}	4.25×10^{-4}

* Values obtained on first heating

Both the enthalpy and entropy change values increase in order:

$$ortho < meta < para$$

On the basis of the calorimetric data, it seems reasonable to compare mesomorphic features of the possible monohalogeno derivatives. In Table III the thermal stability values of cholesteryl benzoate and the monohalogeno derivatives are summarized; as the melting point in the case of non-mesomorphic substances, the thermal stability values well characterize the liquid crystalline phases.

Table III

Thermal Stability Values of the Cholesteryl Benzoates
(°C)

	H	F	Cl	Br	I
Ortho	178.0	173.0	146.0	134.0	112.0
Meta	178.0	171.4	147.0	142.0	130.0
Para	178.0	229.7	257.0	257.0	252.0

The data in Table III show that for the *ortho*- and *meta*-derivatives the thermal stability decreases with increase of the space requirements of the substituent. In the case of the *para*-derivatives such a tendency is not present. At extremely high temperatures all four *para*-substituted compounds give an isotropic liquid, leading to the conclusion that all the mesophases are very stable and therefore their stabilities are not influenced essentially by the nature of the substituent.

Comparing the thermal stability values of the corresponding *ortho*-, *meta*- and *para*-derivatives, it can be seen that the stability changes in the order:

$$ortho < meta < para$$

With the decrease of the space-filling of the substituent, the difference between the thermal stabilities of the *ortho*- and *para*-derivatives decreases. This tendency in the case of the fluoro-derivatives is such that the stability order changes:

$$meta < ortho < para$$

To summarize, we may conclude that on increase of the space-requirement of the halogeno substituent, the thermal stability decreases according to the position of the substituent, in the order:

$$ortho < meta < para$$

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ЖИДКИЕ КРИСТАЛЛЫ, I. СИНТЕЗ И ИССЛЕДОВАНИЕ ХОЛЕСТЕРИЛ-ФТОРОБЕНЗОАТОВ

П. М. Агоч, Г. Мотика, Й. А. Сабо и А. И. Золтаи

Синтетизированы *орто-*, *мета-* и *пара*-фторобензоаты Холестерина. Методом дифференциально-сканирующей калориметрии определены температуры, энтальпии и энтропии фазовых переходов. Оптические свойства изученных производных показывают, что все они являются энантиотропными жидкими кристаллами холестерина.