THERMAL BEHAVIOR OF SOME CHOLESTERIC ESTERS

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Taking into account the importance of thermal stability in the liquid crystals field, the study presents thermal behavior of some cholesteric esters, which differ by the nature of the functional group attached to the cholesteryl unit and the connecting position of the nitro or amino functions to the aromatic ring. The cholesteric esters present liquid crystalline properties, with high melting and clearing points and may be used as intermediates in the synthesis of liquid crystals. Some other kinetic characteristics, such as reaction order (n), activation energy (E_a) and pre-exponential factor ($\ln A$) have been also evaluated. The type of functional units adjacent to the aromatic unit determines thermal stability of the cholesteryl compounds. Groups with a powerful withdrawing effect induce a decreasing of the temperatures at which the material starts to lose mass. An increased thermal stability for the amino esters has been observed, probably because of some intermolecular hydrogen bonds formation.

Keywords: *cholesteryl ester, thermal degradation*

Introduction

Liquid crystals are materials in which the mesomorphic properties appear in a certain temperature domain, so that thermal stability plays an important role for such compounds [1]. For example, in the case of liquid crystals with the clearing point above the decomposition temperature a study of thermo degradation process is requested [2]. Although thermal stability of polymeric liquid crystals was intensively studied [3–7], only a minor attention has been paid to the stability of small molecular liquid crystals [8–13]. Beside this, because of the simplicity of the matrix, such molecules bring the advantage of an easier understanding of the process.

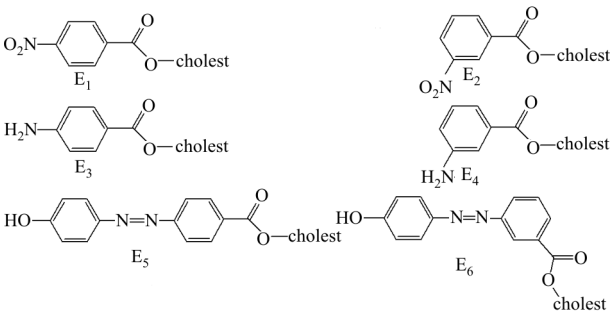
An important factor in inducing thermal stability of cholesteryl esters is the type of functional groups connected to the aromatic unit. The present study is focused on thermal stability of some cholesteric esters that are intermediates in liquid crystals synthesis, with different functional groups attached to the 3rd or 4th-position of the aromatic unit.

The structure of the analyzed compounds is presented in Scheme 1.

Experimental

Materials

All reactions were performed under a dry atmosphere of nitrogen. Silica gel 60 (Merck) or Al_2O_3 (active, neutral, Merck) were used for column chromatography. TLC was performed on silicagel F_{254} or aluminum oxide F_{254} plates (Merck). Dichloromethane was distilled over P_2O_5 prior to use. Dicyclohexylcarbodiimide (Merck), 4-N,N-dimethylamino-pyridine (Fluka), cholesterol (Aldrich), 4-nitrobenzoic acid (Merck), 3-nitrobenzoic acid (Merck) and tin tetrachloride were used as received.



Scheme 1 The structure of the cholesteric esters

Sample preparation

Cholesteryl nitro benzoates synthesis:

To a solution containing 3- or 4-nitrobenzoic acid, cholesterol and a catalytic amount of DMAP in anhydrous CH_2Cl_2, under stirring, a solution of DCC in dried CH_2Cl_2 was added. After 18 h of stirring, the dicyclohexyl urea was filtered off and the solution was concentrated. The solid residue was purified by CC on Al_2O_3 providing pure nitrobenzoates as white solids.

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Cholesteryl- 4-nitro benzoate (E_1):

Quantities: 5 g (29.94 mmoles) 4-nitrobenzoic acid, 11.5769 g (29.94 mmoles) cholesterol, a catalytic amount of DMAP in 150 mL anhydrous CH_2Cl_2, 6.7952 g (32.93 mmoles) DCC in 50 mL anhydrous CH_2Cl_2. Purification: CC on neutral Al_2O_3 (CH_2Cl_2: hexane, 3:1);Yield: 79% (12.67 g), m.p. (liquid crystal): 179°C (K/Ch), 264°C (Ch/I) *m/z*: 534 $[M-1]^+$.

Cholesteryl 3-nitro benzoate (E_2):

Quantities*:* 3.2255 g (19.30 mmoles) 3-nitrobenzoic acid, 7.4627 g (19.30 mmoles) cholesterol, a catalytic amount of DMAP in 100 mL anhydrous CH_2Cl_2, 4.3805 g (32.93 mmoles) DCC in 40 ml anhydrous CH_2Cl_2. Purification: CC on neutral Al_2O_3 (CH_2Cl_2: hexane, 1:1); Yield: 86.04% (8.8974 g), *m.p.* (liquid crystal): 128°C (K/Ch), 170°C (Ch/I);

Cholesteryl amino benzoates

Cholesteryl 4-amino benzoate (E_3):

2 g (3.73 mmoles) cholesteryl p-nitrobenzoate and 8 equiv. of $SnCl_2 \cdot 2H_2O$ (6.739 g, 29.84 mmoles) were refluxed in ethanol (100 ml) for 6 h. After cooling, the mixture was poured over ice water and the pH value was adjusted to 7-8 using a 5% NaOH solution. The mixture was extracted with dichloromethane, washed several times with water and dried over anhydrous $MgSO_4$. After solvent removal, the white solid was purified by column chromatography (Al_2O_3, dichloromethane : hexane, 3:1). Yield: 63.2% (1.2 g), m.p. (liquid crystal): 241°C (K/Ch), decomp; *m/z*:504 $[M-1]^+$.

Cholesteryl 3-amino benzoate (E_4):

1.098 g (16.8 mmoles) of activated zinc (with 20% solution of HCl and washed three times with water and methanol) were added over a solution containing 3 g (5.6 mmoles) cholesteryl 3-nitrobenzoate in 100 mL of dichloromethane. Under vigorous stirring, 2.79 mL of formic acid (80%) was poured in a single portion. The reaction devolves with exothermal effect and powerful foaming. After 15 min of stirring, the reaction is complete and the inorganic compounds are filtered off. The organic solvent was washed several times with a 10% Na_2CO_3 solution and water and dried over $MgSO_4$. The crude product was purified on Silica gel (dichloromethane:ethyl acetate 15:1). Yield: 47.7% (1.35 g), *m.p.*: 184–186°C; *m/z*: 504 $[M-1]^+$.

Azo-cholesteryl mesogens (E_5, E_6)

4-(4-Hydroxy-phenylazo)-benzoic acid cholesteryl ester (E_5):

To a solution of 2 g (3.96 mmoles) of cholesteryl 4-aminobenzoate, dissolved in 30 mL of THF, 0.3 mL of hydrochloric acid (32 %) was added. The mixture was cooled on an ice bath to 0°C and a solution containing 0.3 g (3.96 mmoles) $NaNO_2$ in 2 mL H_2O was dropped, under stirring, keeping the temperature under 5°C. The diazonium salt was maintained at 5°C for additional 30 min. The diazonium salt was added dropwise over a solution containing 0.37 g (3.96 mmoles) phenol and 1.07 g (7.86 mmoles) $CH_3COONa \cdot 3H_2O$, in 5 mL water, at 5°C. After 3 h, the azo derivative was passed over cold water. The orange precipitate was filtered off and washed several times with water. Yield: 84% (2.03 g); *m.p*. (liquid crystal): 190°C (K/Ch), 265°C (Ch/I) decomp; *m/z*: 609 $[M-1]^+$.

3-(4-Hydroxy-phenylazo)-benzoic acid cholesteryl ester (E_6):

To a solution of 0.5 g (0.988 mmoles) cholesteryl 3-aminobenzoate, dissolved in 10 mL of DMF, 0.6 mL (2.66 mmoles) of hydrochloric acid (32%) was added. The mixture was cooled on an ice bath to 0°C and a solution containing 0.07 g (1.1 mmoles) $NaNO_2$ in 0.3 mL H_2O was dropped, under stirring, keeping the temperature under 5°C. The diazonium salt was maintained at 5°C for additional 30 min. The diazonium salt was added dropwise over a solution containing 0.09 g (0.988 mmoles) phenol and 1.0 g (7.35 mmoles) anhydrous sodium acetate, in 4 mL water, at 5°C. After 3 h, the azo derivative was passed over cold water. The orange precipitate was filtered off and washed several times with water. Yield: 50% (0.3 g); *m.p.*: 193°C; *m/z*: 609 $[M-1]^+$.

Methods

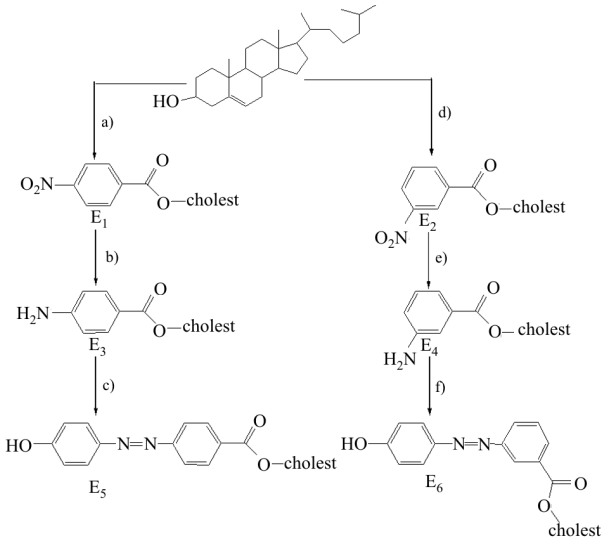
Confirmation of the structures of the intermediates and the final products was obtained by ^{1}H-NMR and ^{13}C-NMR spectroscopy, using a Jeol ECA 600 MHz spectrometer with tetramethylsilane as internal standard. IR spectra were recorded using a Nicolet Magna 550 FT-IR spectrometer (NaCl crystal window). Mass spectra were recorded on a Jeol JMS-AX 505 mass spectrometer (FAB^+ method and as matrix 3-nitro phenyl alcohol).

Thermal behavior of the cholesteryl esters and cholesterol, respectively, was investigated with a MOM-Hungary Derivatograph, which allows simultaneous recording of thermogravimetric, derivative thermogravimetric and differential thermal analysis, in statical air. Aluminum oxide as reference material, calcined at 1000°C, platinum melter, heating rate of 10 K min^{-1} and a sample mass of 26±5 mg have been used.

Kinetic analysis of thermogravimetric data was established using Coats-Redfern integral method [14].

Results and discussion

The performed reactions are shown in Scheme 2:



Scheme 2 The synthesis of cholesteryl esters a – 4-nitrobenzoic acid, DMAP, DCC, CH_2Cl_2, rt; b – $SnCl_2$, ethanol, reflux; c – THF, HCl, $NaNO_2$, 0–5°C, phenol, sodium acetate/water, 0–5°C; d– 3-nitrobenzoic acid, DMAP, DCC, CH_2Cl_2, rt; e– activated zinc, CH_2Cl_2, formic acid, rt.; f – DMF, HCl, $NaNO_2$, 0–5°C, phenol, sodium acetate, 0–5°C

The thermal curves, recorded under the same experimental conditions, are presented in Figs 1–3:
Despite the TG steps for the first mass loss process are not well separated, the DTG curves indicate clearly the overlapping steps. Thus, in the case of E_1, E_2, E_5 and E_6 esters, thermal degradation take place in four stages esters; on the contrary the degradation process for E_3 and E_4 take place in two stages. To study the influence of cholesterol upon the thermal degradation of the investigated esters (E_1, E_2, E_3, E_4, E_5 and E_6), similar thermal curves, in the same conditions has been recorded for cholesterol (Fig 4). It was found out that the thermal degradation of cholesterol starts at 300°C and takes place in four stages.

Table 1 reveals the TG data such as: T_i- the initial temperatures thermal degradation T_{max}– the temperature corresponding to the maximum degradation rate, T_f–the final temperature at which the degradation process for each stage ends, mass loss (m/%), corresponding for each stage, and DTA characteristics (endo or exo).

By analyzing the data from Table 1, one can observe that the thermal degradation process of the investigated compounds starts at around 320°C, the only exception is the E_4 ester, for which T_i =370°C.

For all the analyzed compounds, the most important mass loss was observed in the first stage of thermal degradation. The temperature at which the degradation rate is maximum was situated around 450°C.

In the first stage, thermal degradation of E_3 and cholesterol is much slower as compared to the other compounds, with regard to the temperature interval in which the process takes place (190°C and 220°C, respectively).

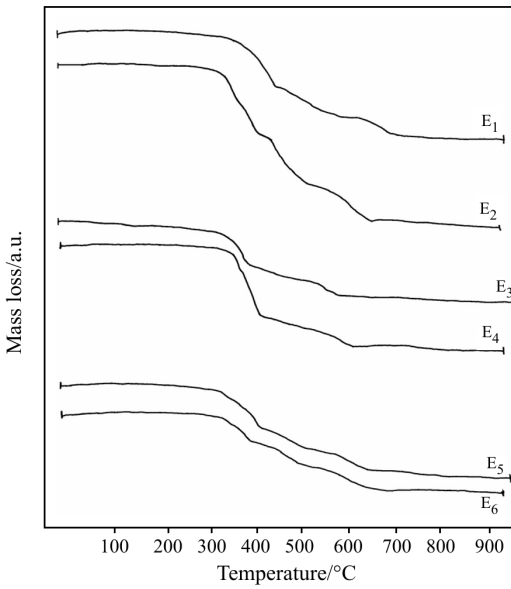


Fig. 1 TG curves of the investigated compounds

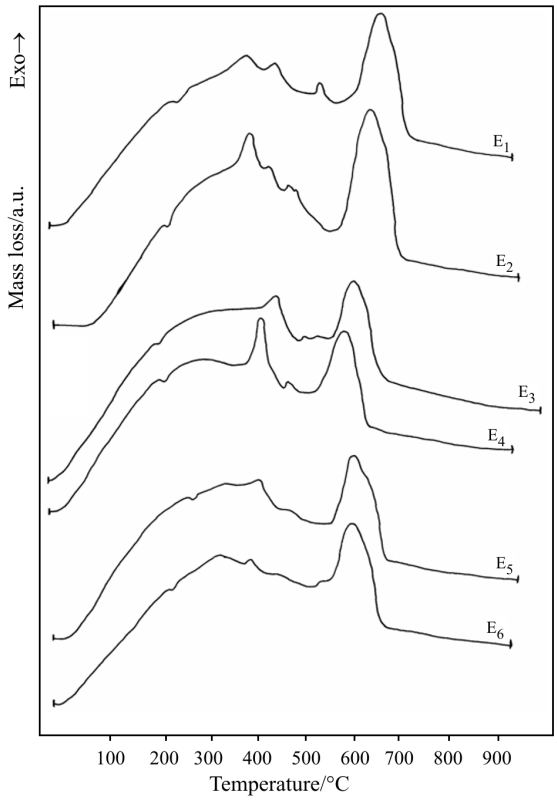


Fig. 2 DTA curves of the investigated compounds

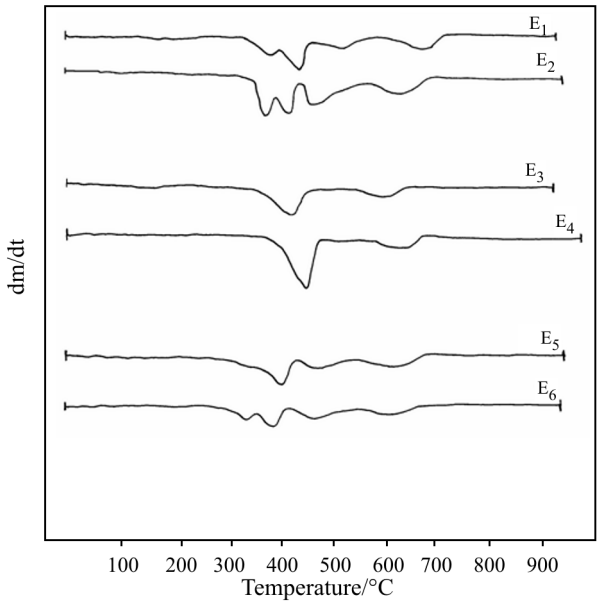


Fig. 3 DTG curves of the investigated compounds

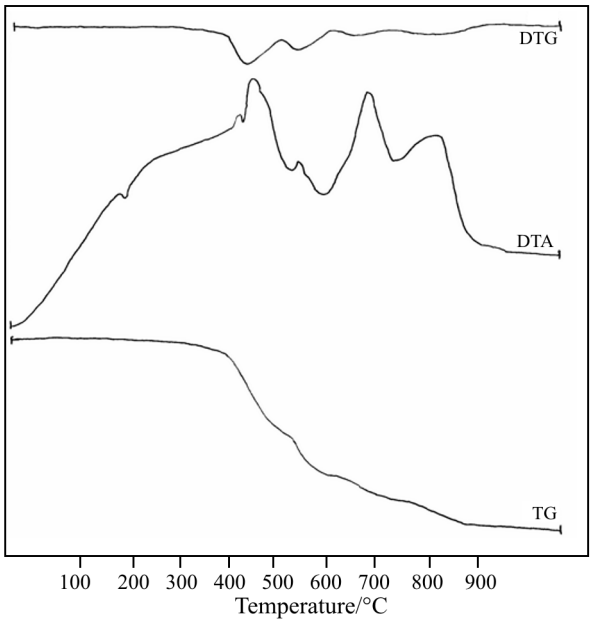


Fig. 4 DTG, DTA and TG curves for cholesterol

Table 1 Thermogravimetric and thermal characteristics

Sample	T_i/°C	T_{max}/°C	T_f/°C	DTA characteristic	Mass loss/%
Stage I					
E_1	320	430	460	exo	55.55
E_2	320	400	480	exo	48.14
E_3	320	425	510	exo	74.07
E_4	370	480	530	exo	73.52
E_5	310	430	460	exo	51.72
E_6	310	450	480	exo	40.74
Cholest	300	440	520	exo	48.37
Stage II					
E_1	460	510	600	exo	27.08
E_2	480	510	640	exo	34.25
E_3	510	600	720	exo	25.93
E_4	530	700	720	exo	26.48
E_5	460	505	620	exo	27.58
E_6	480	530	650	exo	33.33
Cholest	520	540	610	exo	22.32
Stage III					
E_1	600	670	700	exo	17.37
E_2	640	710	740	exo	17.61
E_5	620	660	690	exo	20.70
E_6	650	705	780	exo	25.93
Cholest	610	660	740	exo	13.02
Stage IV					
Cholest	740	800	890	exo	16.29

Table 2 Kinetic characteristics in non-isotherm conditions

Sample	n	E_a /kJ mol^{-1}	ln$A$	r^2
Stage I				
E_1	0	46.10	12.49	0.98
E_2	0	51.88	14.13	0.98
E_3	1	46.33	9.78	0.96
E_4	1	161.28	28.06	0.98
E_5	1	100.41	19.28	0.99
E_6	1	94.28	17.88	0.98
Cholest	1	91.55	17.23	0.99
Stage II				
E_1	1	117.32	18.88	0.97
E_2	1	96.14	16.55	0.96
E_3	1	184.43	28.29	0.97
E_4	0	78.64	13.12	0.99
E_5	2	217.76	33.49	0.97
E_6	2	195.29	29.02	0.99
Cholest	2	389.09	57.57	0.98
Stage III				
E_1	1	335.24	44.67	0.97
E_2	1	255.08	32.74	0.98
E_5	1	261.48	35.62	0.99
E_6	1	232.70	30.05	0.99
Cholest	2	321.62	39.97	0.99
Stage IV				
Cholest	1	288.03	32.26	0.98

Using as thermal stability criteria the initial temperature of decomposition (T_i), the thermal stability series was established as being the following:

$$\text{Cholest}<E_5\cong E_6<E_1\cong E_2\cong E_3<E_4$$

The nature of the functional groups and their connecting position to the aromatic part of the molecule may influence the thermostability. In case of 4-position, regardless to the nature of functional groups, the initial degradation temperature was not influenced. In the case 3-position, the –NH_2 group induces a considerable increase of the initial temperature of degradation, probably because of the hydrogen intermolecular bonds formation, which increase thermostability.

In order to obtain information regarding the degradation mechanism, a kinetic processing of the data, by using the Coats–Redfern integral method, has been made [12]. The obtained results: reaction order (n), activation energy (E_a) and pre-exponential factor (ln$A$) are presented in Table 2.

Closely values of the activation energy for E_1, E_2 and E_3 in the first stage of degradation process indicate a similar thermostability, which is in a good correlation with the observations obtained from the T_i values.

By modifying the nature of the functional groups and their connection position to the aromatic unit one can observe an increase the activation energy. The highest value corresponds to the sample E_4, which is another proof of the premise regarding to the intermolecular bond formation. The values for the next stages indicate some differences in the second stage, with the tendency of homogenizing in the third stage.

The kinetic characteristics suggest the complexity of the thermal degradation through successive reactions, accompanied by exothermal processes, respectively thermo-oxidative reactions. The values of the reaction order confirm the complexity of the degradation reactions. Supplementary proofs regarding the degradation mechanism of the analyzed compounds, the compensation effect has been studied. Accordingly, a graphical representation of ln$A$ as function of E_a has been carried out, the compensation equations are illustrated in Fig 5.

The linear dependence confirms the similar degradation mechanism of the analyzed compounds in the three stages, the slope of the lines being around 0.14.

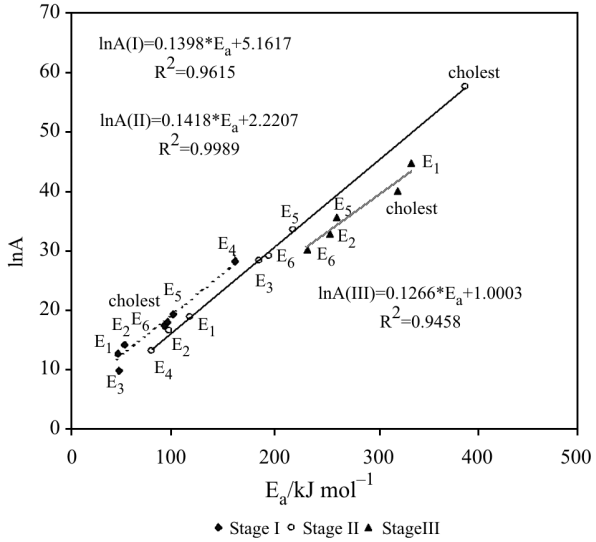


Fig. 5 The pre-exponential factor as function of the activation energy

Conclusions

By applying thermal analysis methods, under dynamic heating conditions, the following conclusions regarding thermostability and the type of the thermal degradation mechanism can be drawn:

- Thermostability varies between 300–370°C, in accordance with the nature and position of the functional groups attached to the aromatic unit;
- The amino functional group in the 3-position as compared to the 4-position induces an important increase in thermostability, probably favored by the hydrogen intermolecular bonds formation;
- The mechanism of thermal degradation is complex, through successive reactions, the important exothermal effects of the process suggesting a thermo-oxidative behavior.

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