

LIQUID CRYSTALS, V*
**SYNTHESIS OF *N*-(ALKOXYCARBONYL-*n*-PENTYL)-3 β -CHOLESTERYL
URETHANES AND THEIR POLYMORPHIC
AND MESOMORPHIC PROPERTIES**

By

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(Received 5th June, 1981)

A homologous series of *N*-(alkoxycarbonyl-*n*-pentyl)-3 β -cholesteryl urethanes has been prepared. The phase transitions have been measured with the aid of differential scanning calorimetry. The textures of the mesophases have been determined with a hot stage equipped polarizing microscope. The phase transition schemes have been described.

Introduction

Liquid crystalline materials with new structures have been prepared, to obtain compounds with favourable mesomorphic properties [1]. An additional object of research is the examination of the connection between the chemical structure and the liquid crystalline properties [2, 3]. We earlier reported [4] the synthesis and mesomorphic properties of a homologous series of *N*-(alkoxycarbonyl-*n*-decyl)-3 β -cholesteryl urethanes, in which ten carbon atoms exist between two different bonding systems (ester and carbamate).

In the compounds described (III/1—III/12) in this publication five carbon atoms exist between the NH group of the carbamate and the carbonyl group of the ester. Accordingly, the change in mesomorphic properties is due to the shortening of the distance between the carbamate and ester groups.

Materials

The synthesis of the compounds was carried out by the reaction of cholesteryl chloroformate (II) and ϵ -aminocaproic acid ester hydrochlorides with the aid of a tertiary amine (Fig. 1). The amino acid esters were synthesized from ϵ -aminocaproic acid and the corresponding alcohols with proton catalysis. The conditions of the synthesis and purifications of the compounds correspond with those in the case of *N*-(alkoxycarbonyl-*n*-decyl)-3 β -cholesteryl urethanes [4]. The physical constants and the analytical data of the compounds prepared are shown in Table I.

*Part IV: P. M. Agócs, G. Motika and P. Zsedényi: Acta Chim. (Budapest), in press.

Table I
Physical data of *N*-(alkoxycarbonyl-*n*-pentyl)-3 β -cholesteryl urethanes

No.	Alkoxy group	Mol. formula	Mol. weight	Analysis (%)	
				Found	Calc.
III/1	Methoxy	C ₃₅ H ₅₉ O ₄ N	557.87	C=75.70 H=10.91	C=75.35 H=10.66
III/2	Ethoxy	C ₃₆ H ₆₁ O ₄ N	571.90	C=75.57 H=10.70	C=75.61 H=10.75
III/3	Propyloxy	C ₃₇ H ₆₃ O ₄ N	585.92	C=75.63 H=10.76	C=75.85 H=10.84
III/4	Butyloxy	C ₃₈ H ₆₅ O ₄ N	599.95	C=75.90 H=11.10	C=76.07 H=10.93
III/5	Pentyloxy	C ₃₉ H ₆₇ O ₄ N	613.97	C=76.02 H=11.10	C=76.29 H=11.00
III/6	Hexyloxy	C ₄₀ H ₆₉ O ₄ N	628.00	C=76.47 H=11.04	C=76.50 H=11.07
III/7	Heptyloxy	C ₄₁ H ₇₁ O ₄ N	642.03	C=76.55 H=11.22	C=76.70 H=11.15
III/8	Octyloxy	C ₄₂ H ₇₃ O ₄ N	656.05	C=76.78 H=11.26	C=76.90 H=11.22
III/9	Nonyloxy	C ₄₃ H ₇₅ O ₄ N	670.08	C=77.21 H=11.16	C=77.08 H=11.28
III/10	Decyloxy	C ₄₄ H ₇₇ O ₄ N	684.11	C=77.35 H=11.27	C=77.25 H=11.34
III/11	Undecyloxy	C ₄₅ H ₇₉ O ₄ N	698.13	C=77.59 H=11.28	C=77.42 H=11.41
III/12	Dodecyloxy	C ₄₆ H ₈₁ O ₄ N	712.16	C=77.36 H=11.58	C=77.58 H=11.46

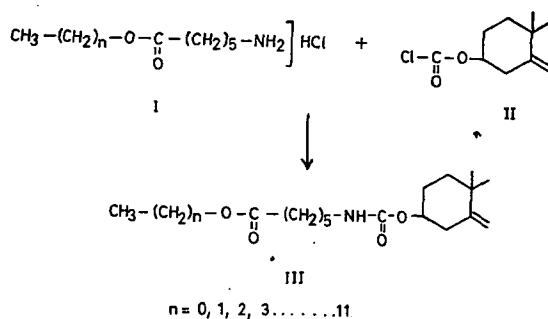


Fig. 1. Synthesis route of *N*-(alkoxycarbonyl-*n*-pentyl)-3 β -cholesteryl urethanes

Results and discussion

The phase transition schemes are shown in Fig. 2. The heating direction is indicated by a continuous line, the cooling direction by a broken line and transitions after thermostating by a dotted line. For the designation of individual states we apply the following abbreviations:

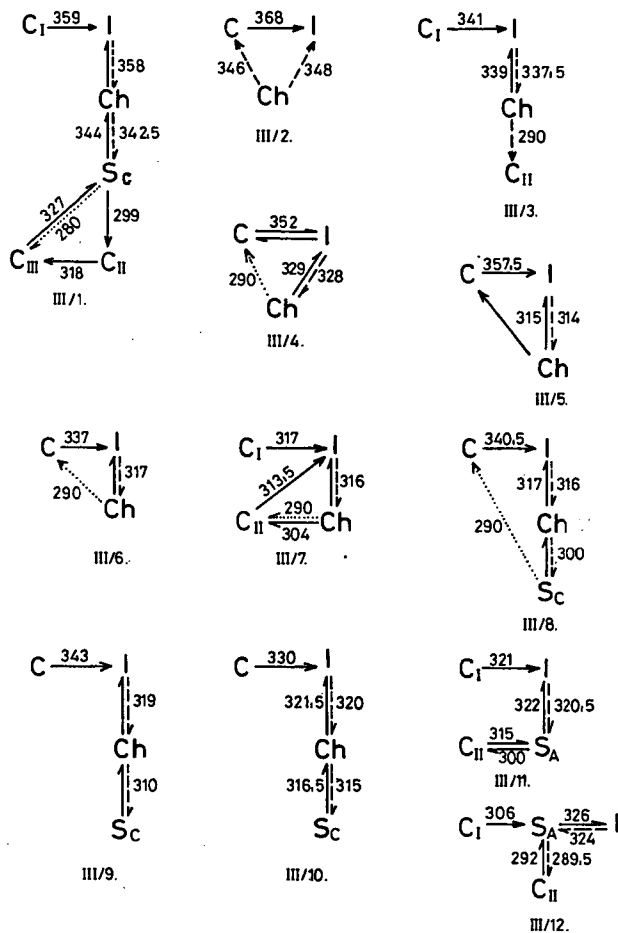


Fig. 2. Phase transition schemes of *N*-(alkoxycarbonyl-*n*-penty)-3 β -cholesteryl urethanes

- I = isotropic liquid
 Ch = cholesteric mesophase
 S_A, S_C = smectic A and C mesophases
 C_I, C_{II}, C_{III} = crystalline modifications

Compound III/1 has S_C and Ch states. The C_I→I transition occurs only in the first heating cycle. The S_C state was cooled to 260 K and did not crystallize, but on thermostating at 280 K for 8–10 hours the C_{III} state was produced. During heating from 260 K, the S_C→C_{II}→C_{III} transitions are observed in the form of two exothermic transitions, at 299 K and 318 K.

Compound III/2 shows a monotropic Ch mesophase, which is followed directly by the crystalline state.

Compound III/3 has a monotropic Ch mesophase and several crystalline polymorphic states. The $C_{II} \rightarrow C_I$ transition does not take place on cooling to 260 K and thermostating at 290 K for several days. However, on heating, the material returns to the starting C_I state via an exothermic and then an endothermic transition.

Compounds III/4, III/5, III/6 and III/7 display a monotropic Ch mesophase. Compounds III/4 and III/5 return to the starting state during thermostating at 290 K for 8–10 hours. Depending on the period of thermostating at 290 K, compound III/5 exhibits 2–4 endothermic and one exothermic phase transitions.

Compounds III/8, III/9 and III/10 have Ch and S_C mesomorphic states. Materials III/9 and III/10 pass from the S_C state to an unidentified modification during thermostating at 290 K.

Compounds III/11 and III/12 form a group which differs significantly from the other materials, for these two compounds alone show an S_A state. With compound III/11 the $S_A \rightarrow C_{II}$ transition does not occur on cooling, but it does take place at 290 K during 30 min., or heating, as an exothermic phase transition.

Fig. 3 shows a plot of the thermal stability and the phase transition temperatures of the prepared compounds against the number of carbon atoms in the alkoxy chain.

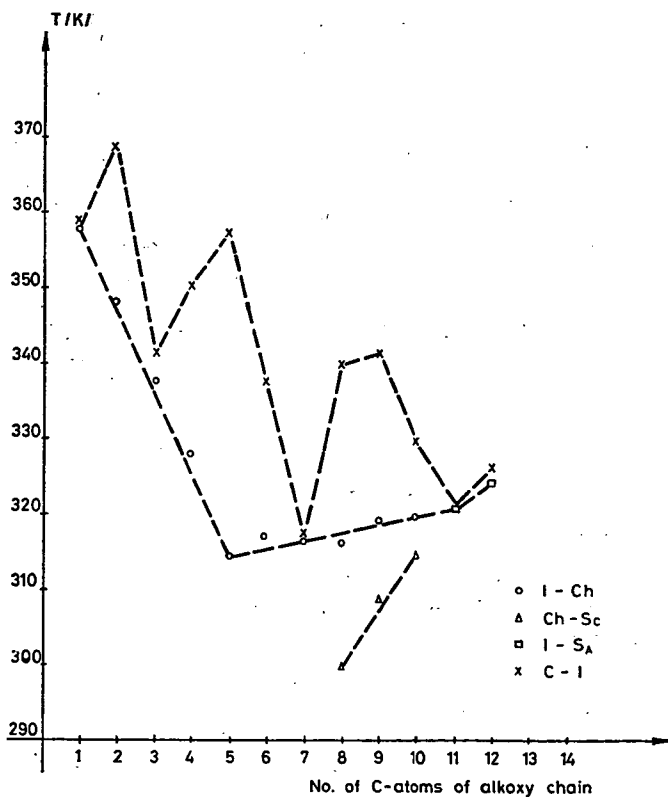


Fig. 3. Transition temperatures of *N*-(alkoxycarbonyl-*n*-pentyl)- 3β -cholesteryl urethanes

To summarize, we may conclude that compounds III/1, III/8, III/9 and III/10 possess Ch and S_C mesophases, compounds III/2, III/3, III/4, III/5, III/6 and III/7 a Ch mesophase, and compounds III/11 and III/12 only an S_A mesophase. The I→Ch transition temperature rapidly decreases from III/2 to III/5, and then moderately increases. The Ch→S_C transition temperature gradually rises with the increase of the number of carbon atoms in the alkoxy chain. The S_A mesophase appears only for the last two members of the series.

Optical and calorimetric measurements

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

The calorimetric measurements were made with a PERKIN—ELMER DSC-2 calorimeter, in highly-purified nitrogen atmosphere. The temperature axis was calibrated with the melting point of indium (99.99%) and the melting point of bidistilled water. The weights of the samples lay in the range 3—5 mg. The temperatures of the phase transitions could be reproduced with an accuracy of ±1 K.

Acknowledgements

The authors are grateful to the Hungarian Technical Development Committee and to the REANAL Chemical Factory for considerable technical assistance and the financial support of this research. Thanks are expressed to Mrs. Dr. Bartók-Bozóki and Mrs. É. Gács-Gergely for the combustion analyses, to Mr. A. Gajdacs for technical assistance, to Dr. Gy. Dombi for the PMR spectra, and to Mr. J. Kiss for the IR spectra and helpful discussions.

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ЖИДКИЕ КРИСТАЛЛЫ, V. СИНТЕЗ N-(АЛКОКСИКАРБОНИЛ-Н-ПЕНТИЛ)-3β-ХОЛЕСТЕРИЛ УРЕТАНОВ И ИЗУЧЕНИЕ ИХ ПОЛИМОРФНЫХ СВОЙСТВ

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Синтезирован гомологический ряд N-(алкоксикарбонил-н-пентил)-3β-холестерил уретанов. Определены фазовые переходы синтезированных веществ методом дифференциально-калориметрической калориметрии. Структура мезофаз определялась с помощью высокотемпературного поляризационного микроскопа. Предложены схемы протекания фазовых превращений.