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Gas chromatographic separation of *cis–trans* isomers of alkylcyclohexylbenzenes on a capillary column with a liquid crystalline stationary phase

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ABSTRACT

Liquid crystal derivatives of cyclohexylbenzene with an isothiocyanate group have interesting properties with respect to application in displays. However, only *trans* isomers of these compounds are useful for this purpose, hence separation of the isomers during synthesis and the determination of the amount of the waste *cis* isomer are necessary. The *cis–trans* isomers can readily be separated and analysed using short (15 m) glass capillary columns coated with a liquid crystalline stationary phase. A liquid crystal derivative with an isothiocyanate group has been applied. For comparison, some chromatographic separations on Hewlett-Packard Ultra-2 column were performed. Because of the specific retention mechanism of the liquid crystalline phase it was possible to separate isomers with better selectivity and in a shorter time than on the Ultra-2 column. However, as a result of its high efficiency, the Ultra-2 column is better for the chromatographic separation of the other by-products of the synthesis.

INTRODUCTION

Trans isomers of alkylcyclohexylbenzene derivatives with an isothiocyanate group are a family of liquid crystal compounds that are attractive for application in displays. The usefulness of these compounds is greater than that of the analogous cyano compounds because of their superior physicochemical properties, *viz.*, a smaller bulk viscosity, smaller bend elastic constants, smaller dipole moment, lower dielectric anisotropy and higher birefringence [1–3]. Liquid crystal isothiocyanates make it possible to obtain a wide assortment of liquid crystalline mixtures revealing good chemical stability and high display dynamics; the method of their synthesis has been published [4].

Liquid crystalline isothiocyanates and intermediate products of their syntheses exist in two isomeric forms, *cis* and *trans*. The final liquid crystal products of the syntheses should not contain *cis* isomers, hence it is necessary to remove *cis* isomers from all the intermediate products and to determine the contents of waste *cis* isomers in the intermediate products.

The *cis* isomers are removed step by step from successive intermediate products by applying different methods such as crystallization, distillation and column liquid chromatography [4].

For the determination of the content of *cis* isomers we applied gas chromatography on a column with a liquid crystalline stationary phase. Liquid crystalline stationary phases provide a unique selectivity for the separation of many classes of isomers whose molecules have different length-to-breadth ratios [5–10]. Considering the high boiling points of the analyte isomers, only liquid crystalline stationary phases having high thermal resistance can be used.

EXPERIMENTAL

Compounds

Intermediate products of liquid crystal syntheses whose *cis–trans* isomers were analysed have the following general formulae:

R-C(=O)-⟨ring⟩-⟨ring⟩

R-⟨ring⟩-⟨ring⟩

R-⟨ring⟩-⟨ring⟩-C(=O)-CH₃
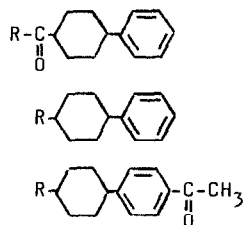
where R = C_1–C_8 alkyl. These compounds were isolated from the reaction mixtures and 0.1–0.4 μl of 1–2.5% solutions in dichloromethane (POCh, Gliwice, Poland) were injected into the gas chromatograph. Some raw reaction mixtures containing all by-products of the syntheses were also analysed.

We also attempted to determine the purity and *cis–trans* isomer contents in the final liquid crystal products of the syntheses. Compounds with the following general formula were analysed:

R-⟨ring⟩-⟨ring⟩-NCS
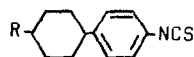
where R = C_2–C_8 alkyl.

Chromatographic procedure

The formula of the 1-[4'-(4-*trans*-pentylcyclohexyl)biphenyl]-2-(4-isothiocyanatophenyl)ethane liquid crystal used as the stationary phase is

C_5H_{11}-⟨ring⟩-⟨ring⟩-⟨ring⟩-CH₂-CH₂-⟨ring⟩-NCS

and the temperatures of the phase transitions are

$$K \underset{\rightleftharpoons}{\overset{135°C}{}} S \underset{\rightleftharpoons}{\overset{163°C}{}} N \underset{\rightleftharpoons}{\overset{280°C}{}} I$$

the phases being the solid crystal (K), smectic mesophase (S), nematic mesophase (N) and isotropic liquid (I). Its synthesis and some of its chromatographic applications have been reported [11–13].

The liquid crystalline stationary phase was deposited statically in a glass capillary column (12 m × 0.3 mm I.D.) according to the procedure described previously [13]. The column efficiency was about 700 theoretical plates/m (capacity factor = 7.53; pyrene; temperature 250°C). Column preparation was performed at Maria Curie-Skłodowska University, Lublin, Poland.

Some analyses were carried out on a fused-silica capillary column (25 m × 0.2 mm I.D.) with a 0.33-μm film of non-mesomorphic Ultra-2 stationary phase (Hewlett-Packard). The column efficiency was 4900 theoretical plates/m (capacity factor = 6.98).

A Pye Unicam (Cambridge, UK) Model GCV gas chromatograph equipped with a split-stream injector and a flame ionization detector was used. The carrier gas was helium and the make-up gas was nitrogen.

RESULTS AND DISCUSSION

The separations of *cis–trans* isomers of alkylcyclohexylbenzenes on a capillary column with a liquid crystalline stationary phase are characterized by high selectivity because of the specific retention

TABLE I

RELATIVE RETENTION TIMES (α) OF *TRANS–CIS* ISOMERS

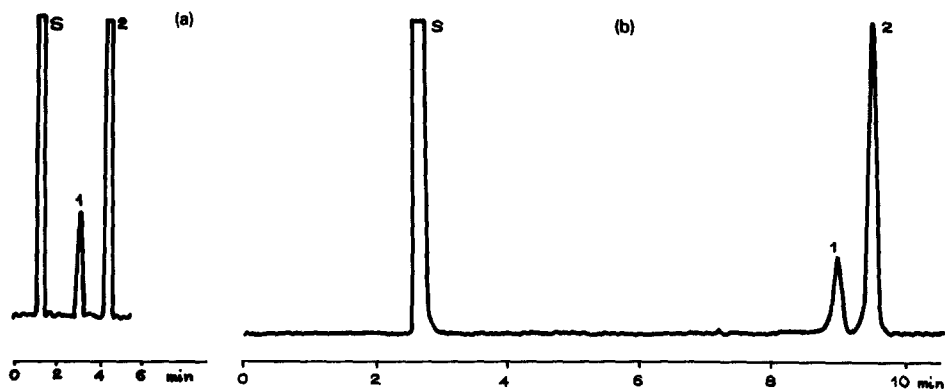| Compound	Column temperature (°C)	α	
		On column with liquid crystal	On column with Ultra-2
C_3H_7-C(=O)-⟨ring⟩-⟨ring⟩	226	1.80	1.09
C_7H_{15}-⟨ring⟩-⟨ring⟩	200	2.18	1.13

Fig. 1. Chromatograms of *cis-trans* isomers of butanoylcyclohexylbenzene. (a) On capillary column with liquid crystalline stationary phase. Column temperature, 226°C; injector and detector temperatures, 340°C; carrier gas (helium) linear velocity, 20 cm/s; make-up gas (nitrogen) flow-rate, 40 cm³/min; splitting ratio, 1:100. (b) On capillary column with Ultra-2 stationary phase. Carrier gas (helium) linear velocity, 16 cm/s; other conditions as in (a). Peaks: 1 = *cis* isomer; 2 = *trans* isomer; S = solvent.

mechanism. The *trans* isomers, having a larger length-to-breadth ratio than the *cis* isomers, were eluted with a longer retention time. Comparison of the separation selectivity (expressed in terms of the relative retention time of *trans* isomers with respect to the *cis* isomers obtained on the two columns indicates an advantage with the use of the column with the liquid crystalline phase. The relative retention times of *trans–cis* isomers of two compounds are given in Table I.
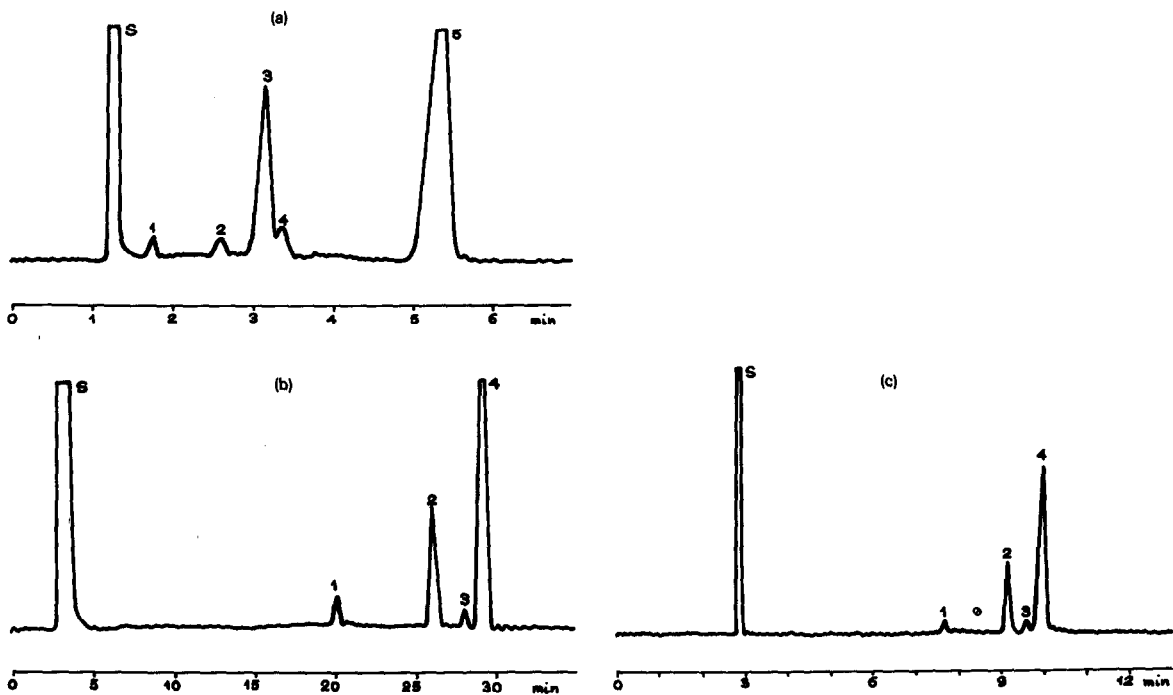

Fig. 2. Chromatograms of *cis–trans* isomers of 4-heptylcyclohexylbenzene. (a) On capillary column with liquid crystalline stationary phase. Column temperature, 200°C; injector and detector temperatures, 320°C; carrier gas (helium) linear velocity 20 cm/s; make-up gas (nitrogen) flow-rate, 40 cm³/min; splitting ratio, 1:100. Peaks: 1,2,4 = unidentified substances; 3 = *cis* isomer; 5 = *trans* isomer; S = solvent. (b) On capillary column with Ultra-2 stationary phase. Carrier gas (helium) linear velocity, 16 cm/s; other conditions as in (a). Peaks: 1,3 = unidentified substances; 2 = *cis* isomer; 4 = *trans* isomer; S = solvent. (c) chromatogram as in (b) obtained at 240°C.
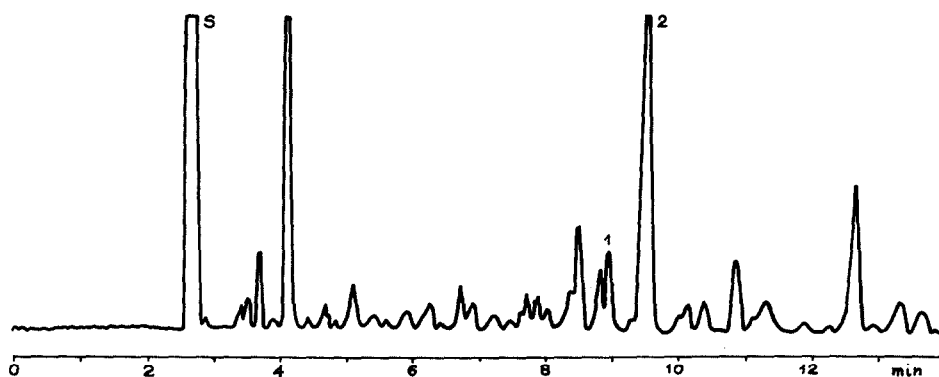
Fig. 3. Chromatogram of reaction mixture after synthesis of butanoylcyclohexylbenzene obtained on a capillary column with Ultra-2 stationary phase. Carrier gas (helium) linear velocity, 16 cm/s; other conditions as in Fig. 1a. Peaks: 1 = *cis* isomer; 2 = *trans* isomer; S = solvent.

The time required to obtain chromatograms on the column with the liquid crystalline phase was considerably shorter than that on the column with Ultra-2 (see Figs. 1 and 2, which show the chromatograms of the *cis–trans* isomers of the substances in the Table I obtained on both columns).

As a result of the much higher efficiency of the Ultra-2 column, the separations of by-products in the raw reaction mixtures after syntheses are better on this column (see Fig. 3).

Examples of the chromatographic separation of

cis–trans isomers of other compounds are shown in Figs. 4 and 5.

An attempt to perform the chromatographic analysis of liquid crystals on the column with the liquid crystalline stationary phase gave negative results. The similarity of the molecular shapes of the stationary phase and the analyte liquid crystals resulted in very high retentions, some retention times even being over 60 min. Under the same conditions the liquid crystals were eluted from the Ultra-2 column in 10–15 min (Fig. 6).
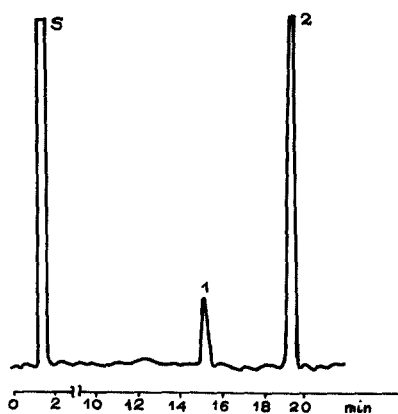

Fig. 4. Chromatogram of *cis–trans* isomers of 4-(4-pentylcyclohexyl)acetophenone on a capillary column with liquid crystalline stationary phase. Conditions as in Fig. 1a. Peaks: 1 = *cis* isomer; 2 = *trans* isomer; S = solvent.
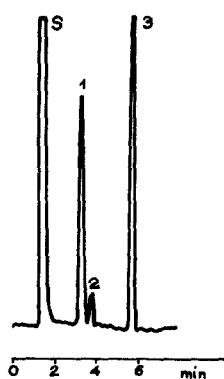

Fig. 5. Chromatogram of *cis–trans* isomers of 4-propylcyclohexylbenzene on a capillary column with liquid crystalline stationary phase. Column temperature, 165°C; other conditions as in Fig. 1a. Peaks: 1 = *cis* isomer; 2 = impurity; 3 = *trans* isomer; S = solvent.
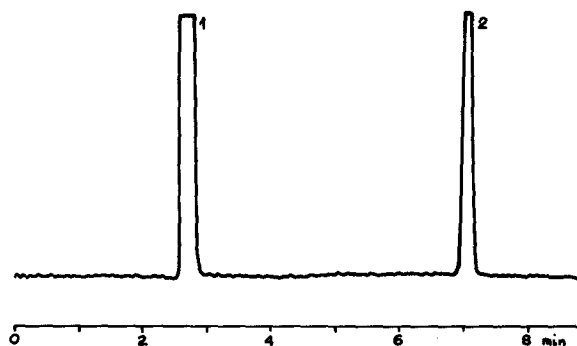
Fig. 6. Chromatographic analysis of the purity of 4-(isothio-cyanatophenyl)-1-(*trans*-4-propyl)cyclohexane on a capillary column with Ultra-2 stationary phase. Column temperature, 280°C injector and detector temperatures, 360°C; carrier gas (helium) linear velocity, 16 cm/s; other conditions as in Fig. 1a. Peaks: 1 = dichloromethane (solvent); 2 = *trans* isomer of liquid crystal.

CONCLUSIONS

The application of a liquid crystalline stationary phase to the chromatographic determination of *cis–trans* isomers of alkylcyclohexylbenzenes allows the analysis time to be shortened in comparison with that on the Ultra-2 column.

The chromatographic separation of raw syntheses mixtures which contain many by-products are better

on the Ultra-2 column. After purification, for checking isomer contents, it is preferable to apply the column with the liquid crystalline stationary phase.

The use of liquid crystalline stationary phases for analysing liquid crystals is unsatisfactory because of very long retention times.

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