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SYNTHESIS AND TESTING OF NEW HIGH-TEMPERATURE LIQUID CRYSTALLINE STATIONARY PHASES

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SUMMARY

Three new liquid crystalline Schiff's bases were synthesized that show wide mesophase ranges. The properties of these compounds as stationary phases and their separating capacities towards polynuclear hydrocarbons were tested.

INTRODUCTION

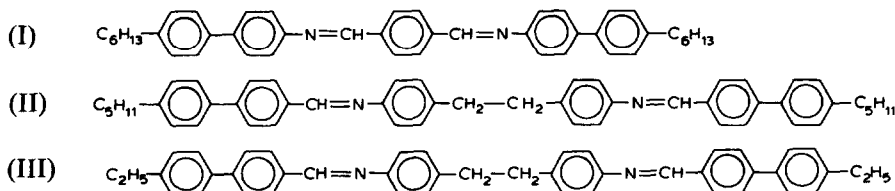
Liquid crystalline stationary phases have been successfully used in the analysis of polynuclear hydrocarbons and their derivatives by gas chromatography¹⁻¹⁸. Some of them are particularly highly valued and are used more commonly than others^{2-14,16}. They find application not only in conventional columns but also in capillary^{8,13,14,16,19} and micropacked columns⁷. Liquid crystalline stationary phases are superior to other types used in the analysis of polynuclear hydrocarbons, their major advantage being high selectivity with respect to isomers of hydrocarbons with up to seven condensed rings³. The temperature stability of many liquid crystalline phases is high: some may be used up to about 290°C³. Among the known types, derivatives of Schiff's bases are the most stable. New possibilities arose, however, when polysiloxane liquid crystals were developed¹⁹.

In this work we synthesized three new high-temperature liquid crystalline stationary phases derived from Schiff's bases and tested their properties, including their separating properties with respect to polynuclear hydrocarbons.

EXPERIMENTAL

Liquid crystalline stationary phases

The stationary phases tested have the following formulae:



These compounds were synthesized according to the following methods.

(I) *Terephthalidene-1,4-bis(4'-hexyldiphenylamine)*. A 14 g (0.0552 mole) amount of 4-hexyl-4'-aminodiphenyl and 3.7 g (0.0276 mole) of terephthalaldehyde were heated for 3 h in 300 cm³ of boiling benzene under an azeotropic head. On cooling, brilliant yellow crystals precipitated, which were filtered off, boiled in methanol and filtered again. The yield of the product (m.p. 148°C) was 13 g (77.8%).

4-Hexyl-4'-aminodiphenyl was obtained according to the method given in ref. 20, and terephthalaldehyde was of commercial grade.

(II) *Bis(4'-pentyldiphenylidene)-1,2-di(4-aminophenyl)ethane*. An 8 g (0.0317 mole) amount of 4-formyl-4'-pentyldiphenyl and 3.4 g (0.01585 mole) of 4,4'-diaminodiphenylethane were heated in 250 cm³ of boiling benzene under an azeotropic head. The yellow precipitate was filtered, boiled in methanol, filtered again and dried. The yield of the product (m.p. 130°C) was 10.1 g (93.5%).

4-Formyl-4'-pentyldiphenyl was obtained according to the method given in ref. 21 and 4,4'-diaminodiphenylethane according to that given in ref. 22.

(III) *Bis(4'-ethyldiphenylidene)-1,2-di(4-aminophenyl)ethane*. An 8.3 g (0.0394 mole) amount of 4-formyl-4'-ethyldiphenyl and 4.2 g (0.0197 mole) of 4,4'-diaminodiphenylethane were heated in 200 cm³ of boiling benzene under an azeotropic head. The precipitate obtained after cooling the mixture was boiled in methanol and filtered. The yield was of the product (m.p. 234°C) 8.9 g (75.4%).

4-Formyl-4'-ethyldiphenyl was obtained analogously to 4-formyl-4'-pentyldiphenyl according to the method given in ref. 21 and 4,4'-diaminodiphenylethane according to that given in ref. 22.

Thermo-optical, X-ray and scanning calorimetric tests showed that the liquid crystals obtained have the following phase transition temperatures: (I) solid (*K*) 148°C, smectic E (*S_E*) 225°C, smectic B (*S_B*) 285°C, smectic A (*S_A*) 400°C (decomp.); (II) *K* 130°C, *S_E* 175°C, *S_B* 316°C, *S_A* 387°C isotropic liquid (*I*); (III) *K* 234°C, *S_E* 261°C, *S_B* 282°C, nematic (*N*) 400°C (decomp.). These temperatures show that the liquid crystals have exceptionally high stabilities of the liquid crystalline phase.

The mesophases of two compounds (I and II) have three modifications of the smectic structure whereas the third compound (III) has two modifications of the smectic structure and the nematic structure. We decided to find which of the liquid crystalline structures that occur have good separating properties with respect to polynuclear hydrocarbons. It is generally assumed that nematic mesophases have better separating properties than smectics. It has been shown, however, that in some instances the smectic may have better separating properties than the nematic¹⁵. This refers especially to smectics with a low degree of ordering (modifications A and C). Highly ordered smectics (*e.g.*, B and E) have inferior separating properties.

The characteristics of the stationary phases tested were determined in the following temperature ranges: (I) 210–330°C, (II) 280–360°C and (III) 220–330°C. These temperature ranges resulted from a desire to include in the measurements as many kinds of mesophases of the stationary phases as possible, but they were also conditioned by the thermal stability of the phases, the phase transition temperatures and the boiling points of the test substances.

Chromatographic columns and chromatograph

The liquid crystals were deposited on Chromaton N AW DMCS of grain size

0.15–0.20 mm in amounts of 5 and 2% (w/w) (with respect to the weight of the support) by evaporation from solution (suspension) in chloroform. A Pye Unicam GCV gas chromatograph was used with a flame-ionization detector; glass columns 1.1 m × 4 mm I.D. were used. Before testing was started the freshly filled columns were conditioned at 250°C for 2 h. Deoxygenated argon was used as the carrier gas.

Testing procedure

The relative retentions of anthracene and phenanthrene were determined in the above temperature ranges and also their separation ratios during heating and cooling of the columns. Usually $4 \cdot 10^{-4}$ cm³ of the anthracene solution in benzene or phenanthrene in *n*-hexane were injected into the column. A stop-watch was used for measuring the retention times. Each measurement was repeated three times. The temperature of the injector and detector was usually 340°C.

The separability of the stationary phases was tested using solutions of polynuclear hydrocarbon mixtures.

RESULTS AND DISCUSSION

Figs. 1–3 show the variation of the separation ratio of anthracene between the stationary phase and the carrier gas with column temperature as determined during heating and cooling of the columns. It can be seen that the melting and crystallization points of the stationary phases differ by several degrees. The significant differences

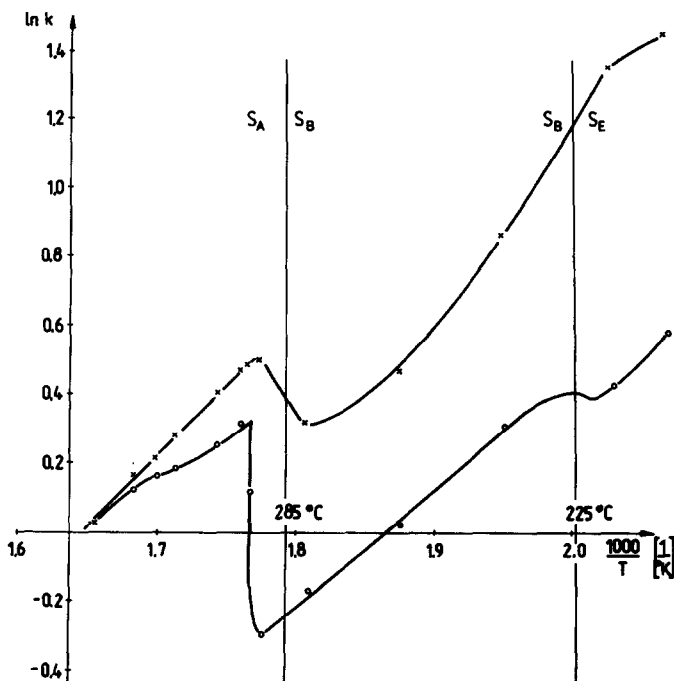


Fig. 1. Variation of the separation ratio with temperature on heating (O) and cooling (X) of the column for phase I (2% on Chromaton N AW DMCS). The temperatures shown were measured thermo-optically.

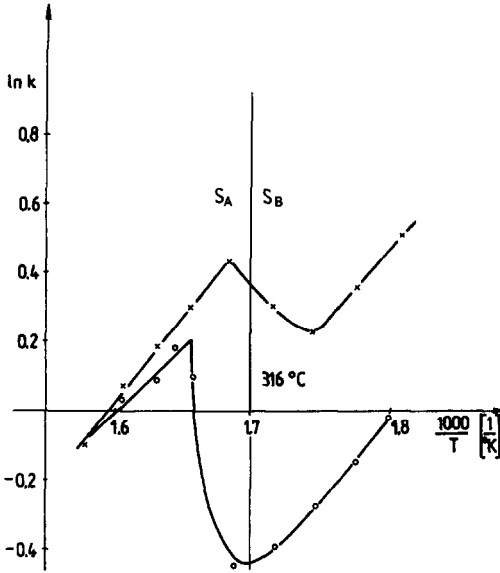


Fig. 2. Variation of the separation ratio with temperature on heating (O) and cooling (x) of the column for phase II (2% on Chromaton N AW DMCS). The temperatures shown were measured thermo-optically.

between the separation ratios for phases I and II as measured during heating and cooling of the columns are of particular interest. These differences are much smaller for phase III, which may be due to the conditions of deposition of the phases on the support (from a suspension rather than solution) and to the conditioning procedure.

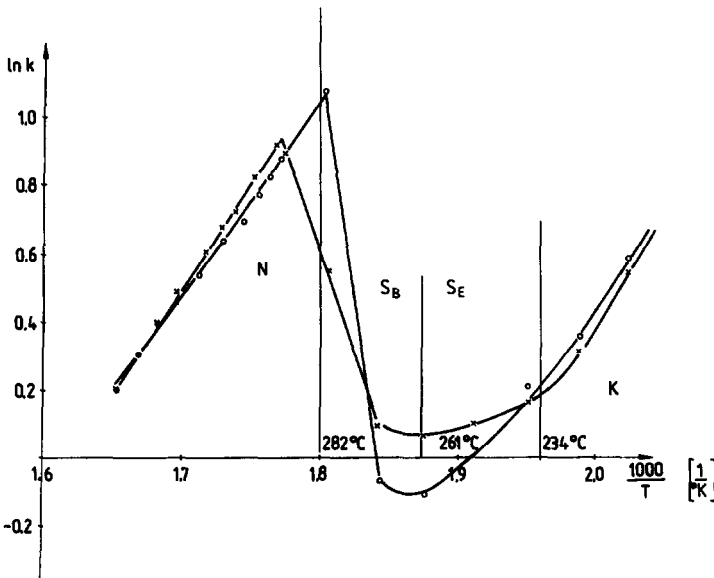


Fig. 3. Variation of the separation ratio with temperature on heating (O) and cooling (x) of the column for phase III (2% on Chromaton N AW DMCS). The temperatures shown were measured thermo-optically.

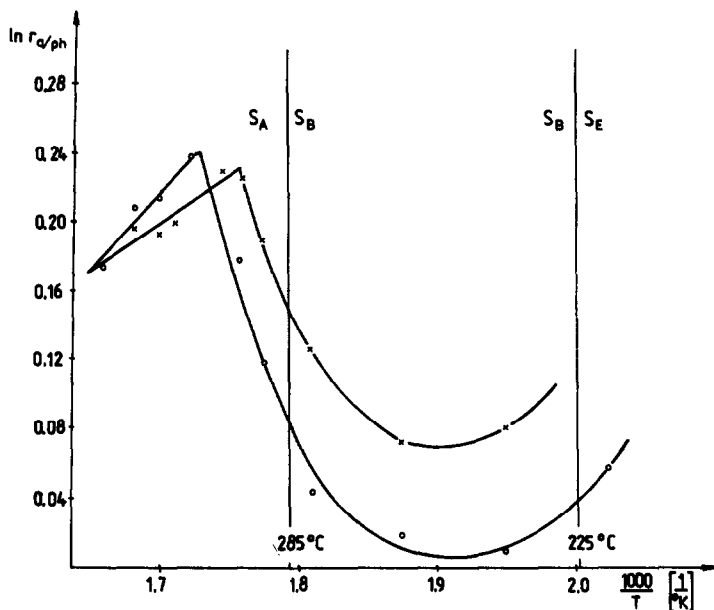


Fig. 4. Variation of the relative retention times of anthracene and phenanthrene with temperature on heating (O) and cooling (\times) of the column for phase I (2% on Chromaton N AW DMCS). The phase transition temperatures shown were measured thermo-optically.

Probably the fact is decisive that the column conditioning temperature (250°C) is removed from the temperature of transition to the less viscous phase, the nematic one with compound III or smectic A with compounds I and II. If the column is heated to the temperature at which the stationary phase has a nematic or smectic A structure, then the separation ratios found during heating and cooling of the columns

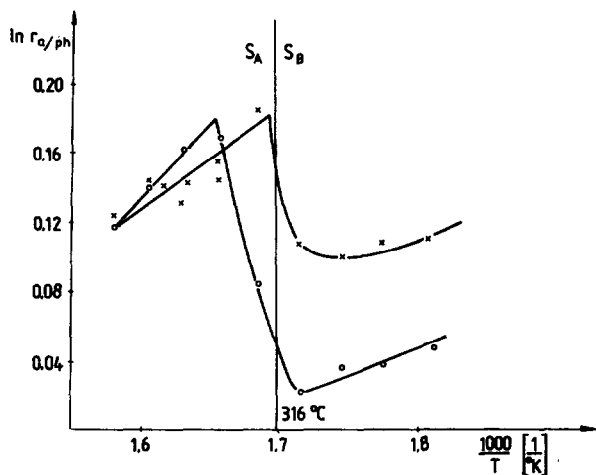


Fig. 5. Variation of the relative retention times of anthracene and phenanthrene with temperature on heating (O) and cooling (\times) of the column for phase II (2% on Chromaton N AW DMCS). The phase transition temperatures shown were measured thermo-optically.

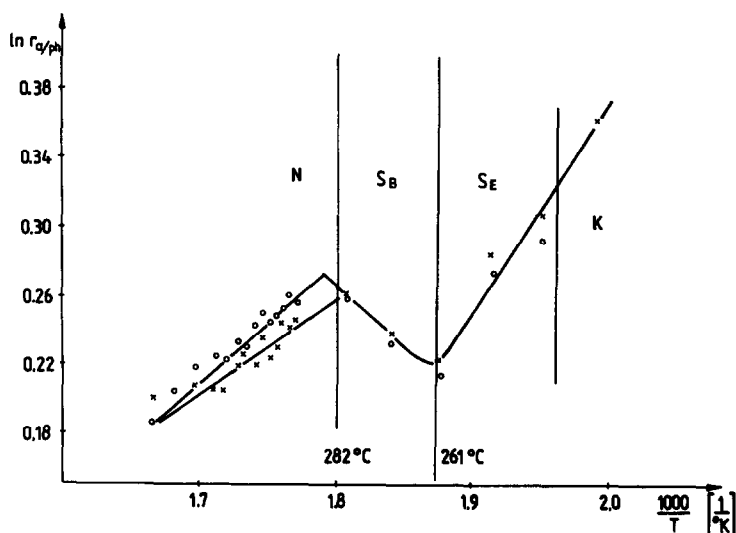


Fig. 6. Variation of the relative retention times of anthracene and phenanthrene with temperature on heating (O) and cooling (x) of the column for phase III (2% on Chromaton N AW DMCS). The phase transition temperatures shown were measured thermo-optically.

are, within the limits of error, the same and close to the values obtained during cooling (Figs. 1–3).

The greatest changes in the separation ratios occur in the region of transition from smectic B to nematic or smectic A. In the region of transition from the solid to the smectic and between the smectics E and B these changes are small. This is due to the greater changes in the structure and viscosity of the stationary phase on transition from smectic B to the nematic or smectic A compared with those which take place on transition from the solid to smectic E and between smectics E and B. The solubility of anthracene in the nematic and smectic A is greater than that in the remaining smectics (B and E) at similar temperatures, *e.g.*, in the phase transition regions. The greater separation ratios observed for phases I and II in the temperature ranges of smectics B and E and solid than in the smectic A range may result from the high adsorption of anthracene on these structural modifications of the stationary phases and on the uncovered support.

Comparison of the relationships shown in Figs. 1–3 indicates that the solubility of anthracene in the nematic is greater than in smectic A.

Figs. 4–6 present the relative retention times ($r_{a/ph}$) of anthracene and phenanthrene over a wide temperature range for heating and cooling of the columns. The relationships lead to conclusions regarding the conditions of initial column conditioning and properties of the stationary phases on the support similar to those drawn from the separation ratios.

The selectivity determined in terms of relative retention for phases I and II (Figs. 4 and 5) is greatest in the region of transition from smectic B to smectic A and has higher values for phase I. With phase III (Fig. 6) in the region of transition from smectic B to the nematic an extreme occurs whose value is higher than that for phase I, but greater selectivity is observed in the temperature ranges of the solid and smectic

E. These ranges are, however, without any greater practical analytical importance, as the chromatographic peaks obtained in these temperature ranges are wide and the real separations are inferior to those obtained in the nematic temperature range. The above refers especially to stationary phases I and II (and to a lesser extent to phase III) for which the wide peaks (symmetric) are accompanied by long retention times.

The components of the test mixture, obtained by dissolution of phenanthrene, anthracene, fluoranthene, pyrene, triphenylene, 1,2-benzanthracene, chrysene, naphthalene, perylene and 3,4-benzopyrene in methylene chloride, were separated on the tested phases. In addition, the components of anthracene oil (semi-product for ob-

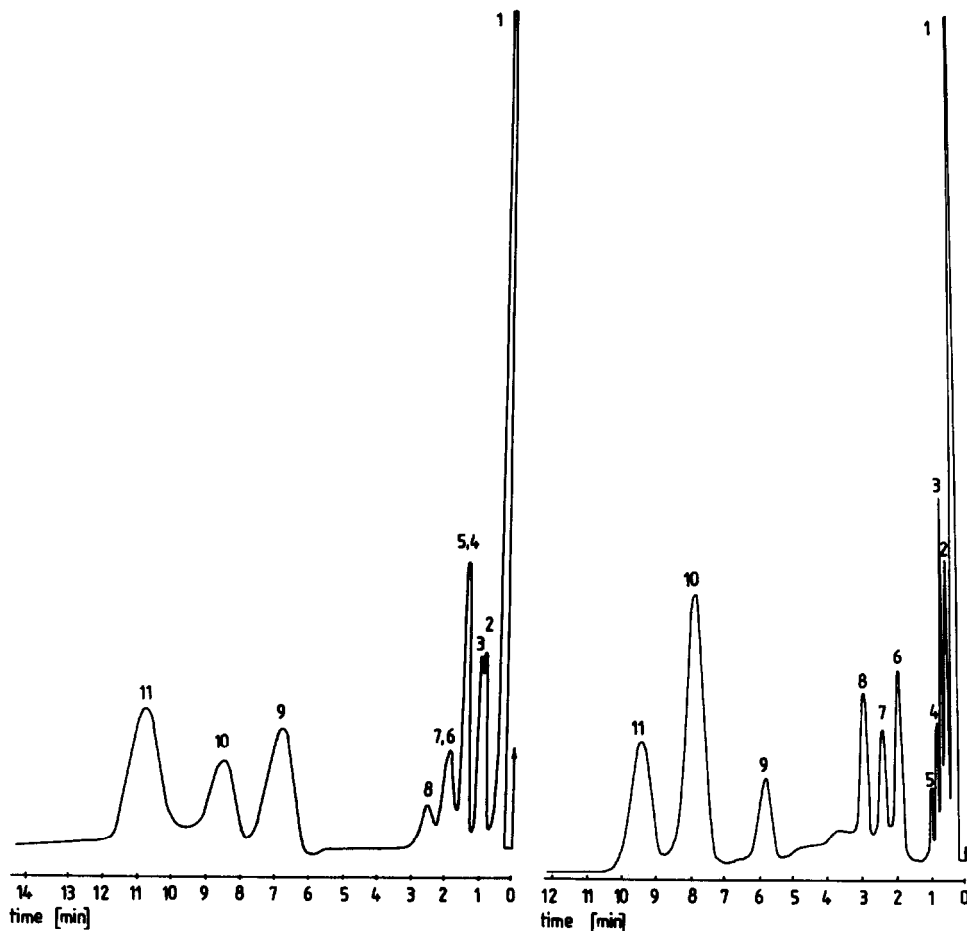


Fig. 7. Separation of hydrocarbon mixture on phase III deposited in an amount of 2% on Chromaton N AW DMCS. Glass column, 1.1 m \times 4 mm I.D.; column temperature, 238°C, detector and injector temperature, 340°C; argon flow-rate, 23.5 cm³/min. Peaks: 1 = benzene; 2 = phenanthrene; 3 = anthracene; 4 = fluoranthene; 5 = pyrene; 6 = triphenylene; 7 = 1,2-benzanthracene; 8 = chrysene; 9 = naphthalene; 10 = perylene; 11 = 3,4-benzopyrene.

Fig. 8. Separation of hydrocarbon mixture on phase III deposited in an amount of 2% on Chromaton N AW DMCS. Column temperature, 282°C. Other conditions, column and separated hydrocarbons as in Fig. 7.

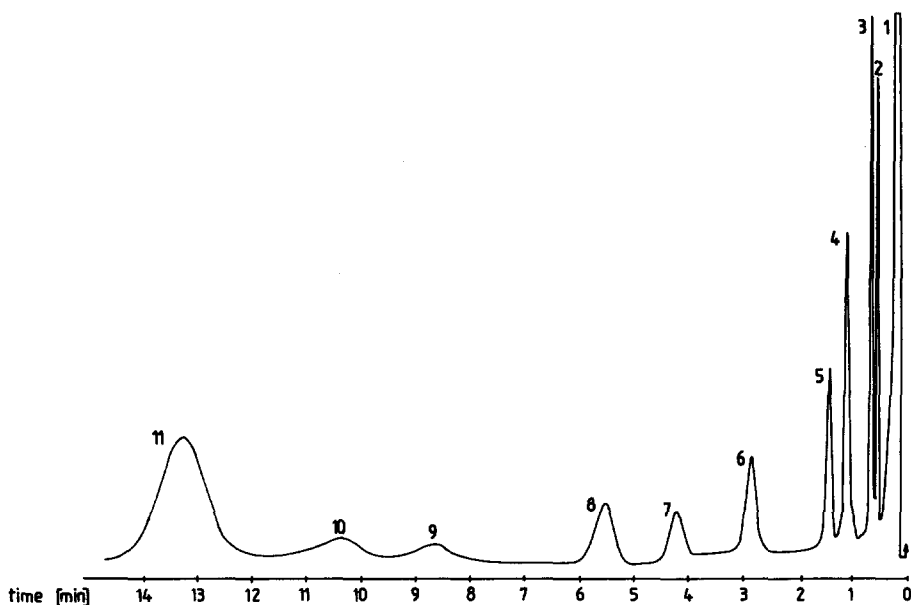


Fig. 9. Separation of hydrocarbon mixture on phase III deposited in an amount of 5% on Chromaton N AW DMCS. Column temperature, 282°C. Other conditions, column and separated hydrocarbons as in Fig. 7.

taining pure anthracene), the methylene chloride extract of carbon black obtained by burning natural gas and the hydrocarbon components of cigarette smoke were separated on these stationary phases.

In Figs. 7 and 8 the separations of a hydrocarbon mixture on stationary phase III deposited on the support in an amount of 2%, carried out at 238°C (smectic E) and at 282°C (nematic), are compared. A better separation was obtained at the higher temperature, the time of analysis being shorter (about 10 min), whereas at the lower temperature the separation time was about 12 min. The separation of the same mixture on stationary phase III deposited on the support in an amount of 5% at 282°C requires about 14 min, the separation being better than when the amount of the phase on the support is smaller (Fig. 9).

Fig. 10 shows the separation of a hydrocarbon mixture on stationary phase II at 316°C (smectic A). The separation is good and is rapid (about 7 min). Fig. 11 shows the chromatogram of a carbon black extract on stationary phase III.

In the ranges of transition to the nematic and smectic A most useful for analytical purposes all the stationary phases show good thermal stability and may be used in practice. At these temperatures the liquid crystals deposited in an amount of 5% on Chromaton N AW DMCS showed no bleeding that might interfere with the analysis. The phases deposited in an amount of 2% on the support may be used at temperatures even about 20–30°C higher than that of the transition to the nematic or smectic A (phase I up to 305°C, II to 330°C and III to 310°C). At the temperatures at which the best separations are obtained, polynuclear hydrocarbons in amounts as small as 10^{-9} – 10^{-10} g can be detected.

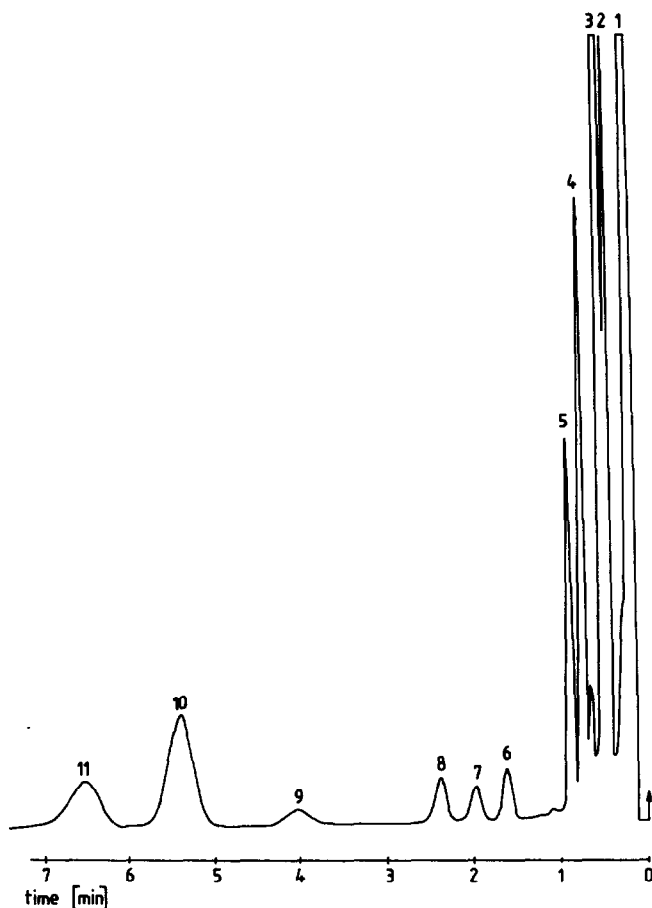


Fig. 10. Separation of hydrocarbon mixture on Phase II deposited in an amount of 5% on Chromaton N AW DMCS. Glass column, 1.1 m \times 4 mm I.D.; column temperature, 316°C; detector and injector temperature, 350°C; argon flow-rate, 46 cm³/min. Separated hydrocarbons as in Fig. 7.

CONCLUSIONS

The liquid crystalline stationary phases obtained in this work can be used at higher temperatures than other liquid crystalline phases. The times of analysis of polynuclear hydrocarbons at these temperatures are shorter than those required with other liquid crystalline stationary phases. Therefore, the stationary phases described here may find application especially in the analysis of higher polynuclear hydrocarbons. The total mesophase temperature range with the tested phases is wide, but the practically useful range is narrower and limited to the smectic A or nematic mesophases, as the highly ordered smectics B and E have only limited application in the analysis of polynuclear hydrocarbons.

The usefulness of the stationary phases for separating mixtures of polynuclear hydrocarbons increases in the order I < II < III.

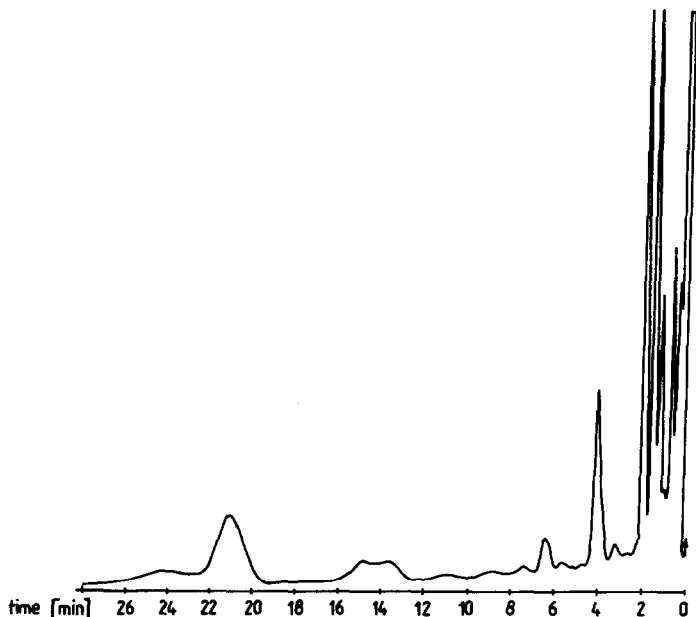


Fig. 11. Chromatogram of carbon black extract on phase III deposited in an amount of 2% on Chromaton N AW DMCS. Glass column, 1.1 m \times 4 mm I.D.; column temperature, 282°C, injector and detector temperature, 340°C; argon flow-rate, 30 cm³/min.

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REFERENCES

- 1 H. D. Sauerland and M. Zander, *Erdöl Kohle, Erdgas, Petrochem. Brenst.-Chem.*, 25 (1972) 526.
- 2 G. M. Janini, K. Johnston and W. L. Zielinski, Jr., *Anal. Chem.*, 47 (1975) 670.
- 3 G. M. Janini, G. M. Muschik, J. A. Schroer and W. L. Zielinski, Jr., *Anal. Chem.*, 48 (1976) 1879.
- 4 G. M. Janini, G. M. Muschik and W. L. Zielinski, Jr., *Anal. Chem.*, 48 (1976) 809.
- 5 G. M. Janini, B. Shaikh and W. L. Zielinski, Jr., *J. Chromatogr.*, 132 (1977) 136.
- 6 J. W. Strand and A. W. Andren, *Anal. Chem.*, 50 (1978) 1509.
- 7 F. Janssen, *Anal. Chem.*, 51 (1979) 2163.
- 8 W. L. Zielinski, Jr. and G. M. Janini, *J. Chromatogr.*, 186 (1979) 237.
- 9 A. Radecki, H. Lamparczyk, J. Grzybowski and J. Halkiewicz, *Z. Anal. Chem.*, 303 (1980) 397.
- 10 G. M. Janini, R. I. Sato and G. M. Muschik, *Anal. Chem.*, 52 (1980) 2417.
- 11 H. J. Issaq, G. M. Janini, B. Poehland, R. Shipe and G. M. Muschik, *Chromatographia*, 14 (1981) 655.
- 12 L. Zoccolillo, G. Goretti and M. Ronchetti, *Chromatographia*, 15 (1982) 757.
- 13 F. Janssen and T. Kalidin, *J. Chromatogr.*, 235 (1982) 323.
- 14 W. L. Zielinski, Jr., R. A. Scanlan and M. M. Miller, *J. Chromatogr.*, 209 (1981) 87.
- 15 J. E. Haky and G. M. Muschik, *J. Chromatogr.*, 214 (1981) 161.
- 16 R. C. Kong, M. L. Lee, Y. Tominaga, R. Pratap, M. Iwao, R. N. Castle and S. A. Wise, *J. Chromatogr. Sci.*, 20 (1982) 502.
- 17 K. Kubica and Z. Witkiewicz, *J. Chromatogr.*, 241 (1982) 33.
- 18 Z. Witkiewicz and A. Waclawczyk, *J. Chromatogr.*, 173 (1979) 43.

- 19 R. C. Kong, M. L. Lee, Y. Tominaga, R. Pratap, M. Iwao and R. N. Castle, *Anal. Chem.*, 54 (1982) 1802.
- 20 R. Dąbrowski and E. Żytyński, *Biul. Wojsk. Akad. Tech.*, 30, No. 6 (1981) 143.
- 21 R. Dąbrowski and E. Żytyński, *Biul. Wojsk. Akad. Tech.*, 30, No. 6 (1981) 161.
- 22 J. Dziaduszek, T. Szczuciński, A. Waclawczyk and Z. Witkiewicz, *Biul. Wojsk. Akad. Tech.*, 28, No. 6 (1979) 73.