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## DISC-LIKE LIQUID CRYSTALLINE STATIONARY PHASES FROM THE TRIPHENYLENE DERIVATIVES GROUP

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### SUMMARY

Disc-like liquid crystals belonging to the triphenylene derivatives group have been tested as stationary phases. Some relationships were determined as a function of the column temperature and separations a few substances were studied. Differences were found in the behaviour of disc-like and rod-like liquid crystalline stationary phases. On disc-like liquid crystals, compounds with a linear molecular structure are easily separated from those with a cyclic structure having similar boiling temperatures.

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### INTRODUCTION

Liquid crystalline stationary phases are gaining ever increasing significance in gas chromatography, as confirmed by the large number of publications devoted to the testing of the properties and analytical applications of these stationary phases. The analytical results obtained are very promising, and gas chromatography is suitable for testing certain physico-chemical properties of liquid crystals<sup>1-21</sup>.

So far nematic, cholesteric and smectic liquid crystals with molecules of elongated structure have been studied. The high selectivity of these liquid crystals is related to the ordered arrangement of their molecules. Thanks to this ordering, chromatographed compounds whose ratio of molecule length to width is greater are better dissolved and longer retained in the column than those for which this ratio is smaller. Likewise, the flatter is the molecule, the longer it is retained in the column.

Among known liquid crystals, the group most recently discovered are disc-like liquid crystals. The structure of their molecules differs significantly from that of those known earlier. The disc-like liquid crystals have flat molecules in which neither the length nor the width is distinguished. These compounds are most often hexasubstituted derivatives of benzene, triphenylene or truxene<sup>22-27</sup>.

The properties of disc-like liquid crystals are not well known and as yet they have not been tested as stationary phases in gas chromatography. We therefore decided to undertake investigations of the properties of these liquid crystals as stationary phases, expecting that they might have some properties different from those of other liquid crystal stationary phases known hitherto. The literature indicated that

disc-like liquid crystals dissolve in very different ways compounds with molecules that differ in shape, *e.g.*, xylene isomers<sup>28</sup>. We decided to check whether this is reflected in the properties of these liquid crystals when applied as stationary phases in gas chromatography.

In this work we decided to synthesize liquid crystals from triphenylene derivatives, to investigate their general physico-chemical properties and some of their properties when applied as stationary phases and to carry out separations of selected mixtures.

## EXPERIMENTAL

### *Synthesis of the disc-like liquid crystals*

The synthesis of the disc-like liquid crystals was carried out using hexahydroxytriphenylene and a suitable acid chloride or amyl iodide as the substrates.

Hexahydroxytriphenylene was obtained from hexamethoxytriphenylene in a splitting reaction with hydrobromic acid<sup>29</sup>. Hexamethoxytriphenylene was synthesized from veratrole (*o*-dimethoxybenzene). The method of Musgrave and Webster<sup>30</sup>, consisting in oxidation of veratrole with quinone, or the method of Piatelli *et al.*<sup>31</sup>, consisting in dehydrogenation of veratrole with iron(III) chloride, was used for this purpose.

### *Preparation of triphenylene hexa-4-octylbenzoate (THOB)*

A portion of 0.005 mole (1.6 g) of hexahydroxytriphenylene was dissolved in 50 cm<sup>3</sup> of anhydrous pyridine, 0.033 mole (8.25 g) of *p*-octylbenzoyl chloride was added and the contents were left to stand for 24 h at room temperature. Next, the solution was poured into 500 cm<sup>3</sup> of water acidified with hydrochloric acid. The precipitate was filtered off and after drying dissolved in a small amount of benzene. The solution was passed through a column filled with silica gel, benzene being used as the eluent. After evaporation of the solvent the precipitate obtained was crystallized from isopropyl alcohol as a white substance with the following phase transition temperatures (°C): K  $\frac{137}{\text{---}}$  D  $\frac{201.6}{\text{---}}$  N<sub>D</sub>  $\frac{206}{\text{---}}$  I (K = solid crystal, D = columnar phase, N<sub>D</sub> = nematic phase, I = isotropic liquid) (literature: K  $\frac{179}{\text{---}}$  N<sub>D</sub>  $\frac{192}{\text{---}}$  I<sup>23</sup>; K  $\frac{208}{\text{---}}$  N<sub>D</sub>  $\frac{210}{\text{---}}$  I<sup>24</sup>).

The 4-octylbenzoyl chloride used in the reaction was obtained from 4-*n*-octylbenzoic chloride and thionyl chloride.

### *Preparation of triphenylene hexa-4-heptylbenzoate (THHB)*

The liquid crystal was obtained from hexahydroxytriphenylene and 4-heptylbenzoyl chloride in an analogous manner to THOB. The white substance obtained had the following phase transition temperatures (°C): K  $\frac{177}{\text{---}}$  D  $\frac{235}{\text{---}}$  I (literature: K  $\frac{130}{\text{---}}$  D  $\frac{210}{\text{---}}$  I<sup>23</sup>; K  $\frac{210}{\text{---}}$  I<sup>24</sup>).

### *Preparation of triphenylene hexaenanthate (THE)*

This compound was obtained in an analogous manner to THOB by the reaction of hexahydroxytriphenylene with enanthoyl chloride. The resulting white sub-

stance had the following phase transition temperatures ( $^{\circ}\text{C}$ ): K  $\frac{106}{108}$  D  $\frac{117}{120}$  I (literature: K  $\frac{108}{120}$  D  $\frac{120}{125}$  I<sup>25</sup>).

*Preparation of hexapentyloxytriphenylene (HPT)*

A portion of 0.0075 mole (2.4 g) of hexahydroxytriphenylene was dissolved in 1000 cm<sup>3</sup> of cyclohexanone and 0.045 mole (9 g) of amyl iodide and 0.045 mole (6.2 g) of anhydrous potassium carbonate were added. The contents were heated under reflux for 5 h and then cyclohexanone was distilled off with steam. The precipitate was filtered off and, after cooling, dissolved in chloroform. The chloroform solution was passed through a column of silica gel using chloroform as eluent. The precipitate obtained, after evaporation of chloroform, was crystallized from ethanol. The resultant white product had the following phase transition temperatures ( $^{\circ}\text{C}$ ): K  $\frac{65}{69}$  D  $\frac{118}{122}$  I (literature: K  $\frac{69}{122}$  D  $\frac{122}{125}$  I<sup>25</sup>).

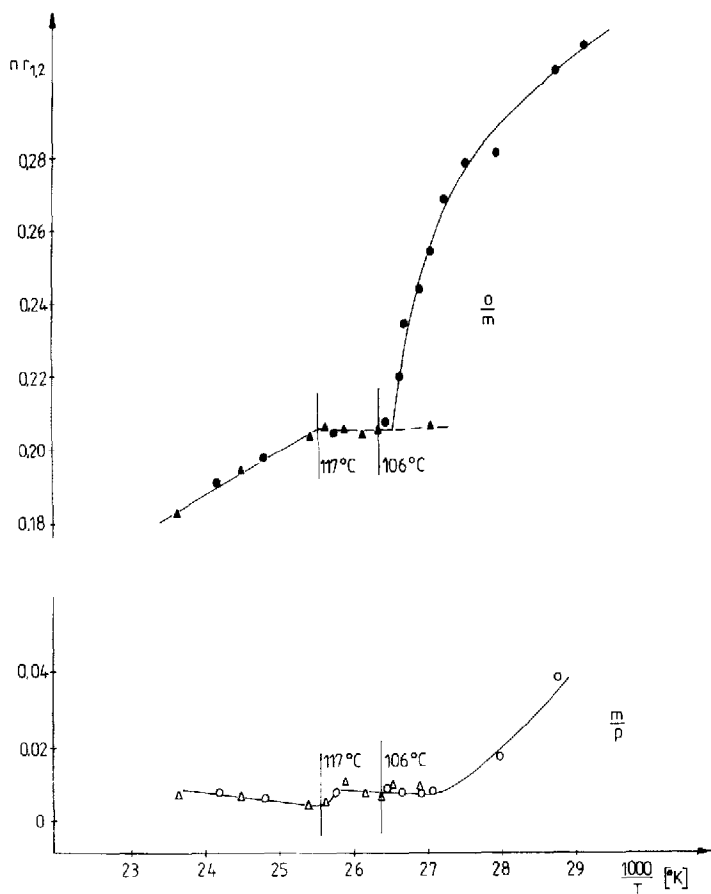


Fig. 1. Dependence of the relative retention time of xylene isomers on column temperature for THE phase deposited on Chromosorb W AW in an amount of 10%. ● and ○, heating; ▲ and △, cooling.

The phase transition temperatures were measured by means of a scanning calorimeter and a polarization microscope with a heated stage.

Elemental analysis of the synthesized compounds confirmed their expected structures.

The purity of the obtained semi-products and liquid crystals was tested by thin-layer chromatography. The final purity of the liquid crystals was checked by high-performance liquid chromatography.

### Chromatographic tests

Two of the synthesized disc-like liquid crystals were classified as low-temperature (HPT and THE) and two as high-temperature types (THOB and THHB). This classification is based on their melting points and mesophase ranges.

The liquid crystals were deposited on Chromosorb W AW in amounts of about 10% and on Chromosorb P HMDS in amounts of about 2% from a chloroform solution. The fillings thus prepared were introduced into 2.1 m  $\times$  4 mm I.D. glass columns. The tests were carried out using a Pye Unicam GCV gas chromatograph with a flame-ionization detector.

Before starting the tests with the low-temperature phases the columns were conditioned for several hours at 140°C. Xylene isomers, cyclooctane and *n*-alkanes with similar boiling points were used as the test substances. With the high-temper-

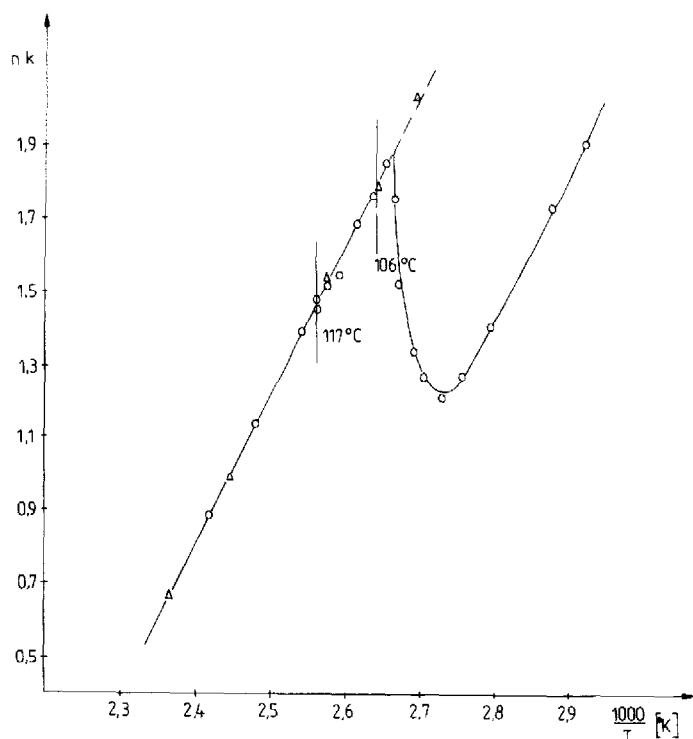


Fig. 2. Temperature dependence of the capacity ratio of *m*-xylene for THE phase deposited on Chromosorb W AW in an amount of 10%. ○, heating; Δ, cooling.

ature phases the columns were conditioned at 240°C and decalin isomers and also phenanthrene and anthracene were used as the test substances.

When testing the temperature dependence of the quantities characterizing the disc-like liquid crystalline stationary phases, the measurements were made in the heating and cooling cycles.

## RESULTS AND DISCUSSION

Figs. 1-4 shows plots obtained for the THE phase. The temperature dependences of the relative retention times of xylene isomers are compared in Fig. 1. The character of these relationships is different than that for most rod-like liquid crystalline stationary phases. With these stationary phases the xylene isomers are usually eluted from the column in the order *m*-, *p*-, *o*-. Rod-like nematic phases show the highest selectivity towards the components of the mixtures to be separated in the mesophase range and the maximum selectivity appears several degrees above the melting point.

With disc-like liquid crystalline stationary phases the xylene isomers are eluted in an order dependent on their boiling point, which is characteristic of most conventional stationary phases. In addition, the relative retention times of isomers are higher in the solid-state temperature range than in the mesophase range, in which they depend only slightly on temperature. The phase transition temperatures of disc-like

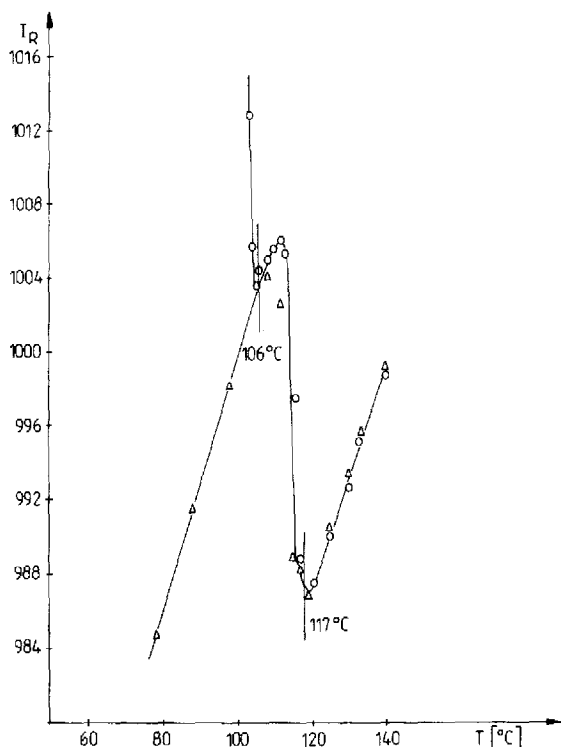


Fig. 3. Temperature dependence of the retention index of cyclooctane on THE phase deposited on Chromosorb W AW in an amount of 10%. Key as in Fig. 2.

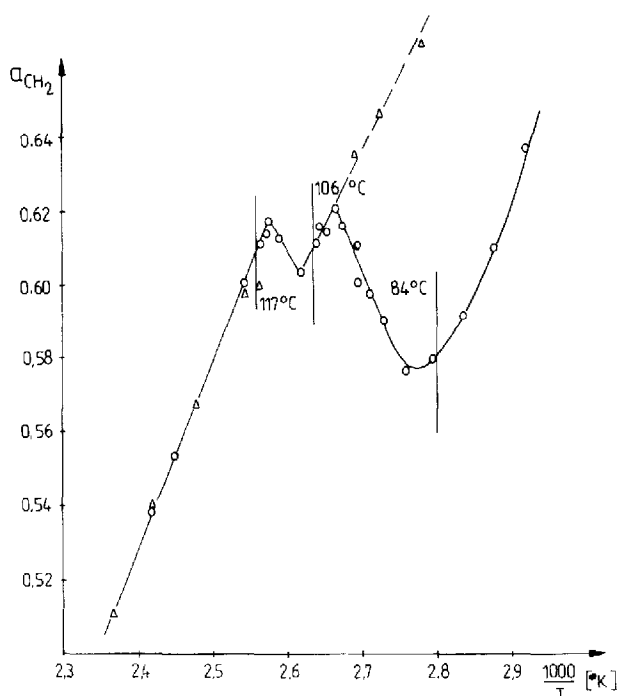


Fig. 4. Temperature dependence of methylene group increment on THE phase deposited on Chromosorb W AW in an amount of 10%. Key as in Fig. 2.

liquid crystals determined chromatographically differ more from those determined thermo-optically than in the case of rod-like liquid crystals. This observation is confirmed by Fig. 2, where the variation of the separation ratio of *m*-xylene with temperature is presented. The melting point of the stationary phase found from the plot is 102°C and differs significantly from that determined calorimetrically (106°C). The course of this relationship also differs from that for rod-like stationary phases, which is demonstrated by the lack of observable effects at the point of transition to the isotropic liquid.

Fig. 3 shows the temperature dependence of the cyclooctane retention index. The phase transition temperatures differ from those determined thermo-optically (in both the column heating and cooling cycles), and vary from those determined for xylenes. From Fig. 3 we can conclude that the retention index depends strongly on temperature and thus on the phase state of the liquid crystal. Comparison of the retention of cyclooctane (b.p. 148.5°C) with that of nonane (b.p. 150.5°C) shows that cyclooctane reacts more strongly with the disc-like structure of the liquid crystal and is eluted from the column second. The reaction of cyclooctane molecules with the disc-like molecules is weaker than that of *n*-alkanes in the isotropic liquid.

The dependence of the *n*-alkane methylene group (increment *a*) on the temperature of the column filled with THE is shown in Fig. 4. The relationship obtained not only allows us to determine the melting and clearing points but also to draw conclusions about the strong but at the same time varying (depending on the phase state) interaction of the *n*-alkane molecules with those of the disc-like liquid crystal.

The regularities found for THE were confirmed with HPT. The characteristic properties of the disc-like liquid crystalline stationary phases are here even more distinct than for THE. The temperature dependence of cyclooctane retention indices presented in Fig. 5 shows that the change in these retention indices is greater than with THE, and a particularly large difference in the values is observed between the beginning of the mesophase and the isotropic liquid.

Fig. 6a shows the temperature dependence of the capacity ratio of cyclooctane for HPT and the carrier gas and in Fig. 6b that of the *n*-alkane methylene group retention. In both instances only the temperature of transition from the mesophase to the isotropic liquid can be determined from the plots, irrespective of whether the plots were obtained in the column heating or cooling cycle. This may indicate that

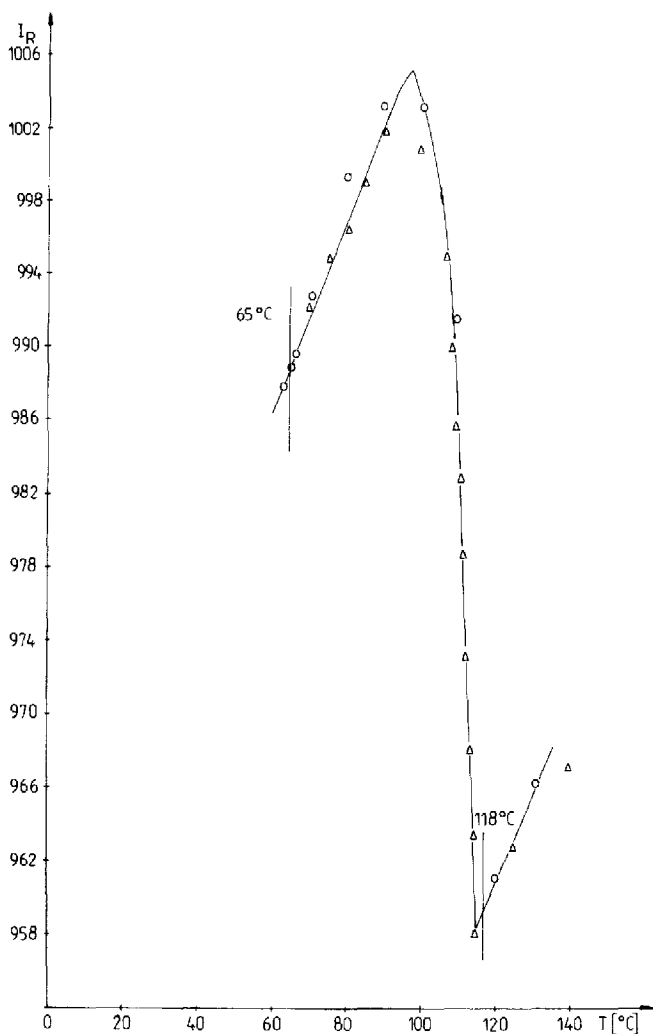


Fig. 5. Temperature dependence of the retention index of cyclooctane on HPT phase deposited on Chromosorb W AW in an amount of 10%. Key as in Fig. 2.

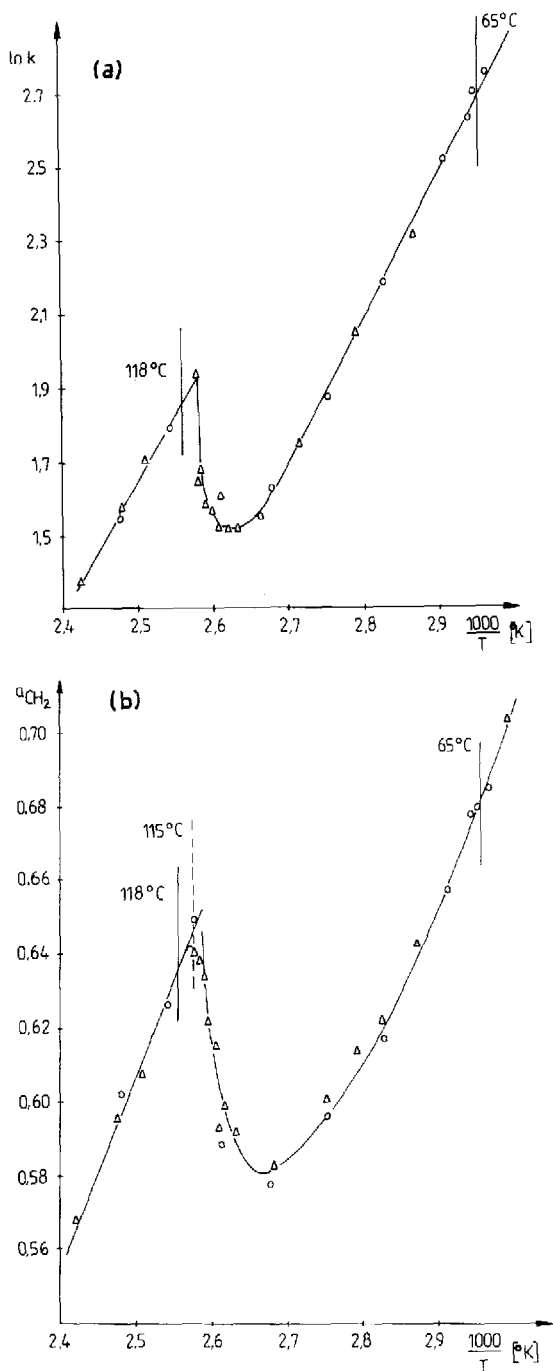


Fig. 6. (a) Temperature dependence of the capacity ratio of cyclooctane on HPT phase deposited on Chromosorb W AW in an amount of 10%. (b) Temperature dependence of methylene group increment on HPT phase deposited on Chromosorb W AW. The dashed vertical line indicates the temperature obtained calorimetrically during cooling the liquid crystal without a support. Key as in Fig. 2.



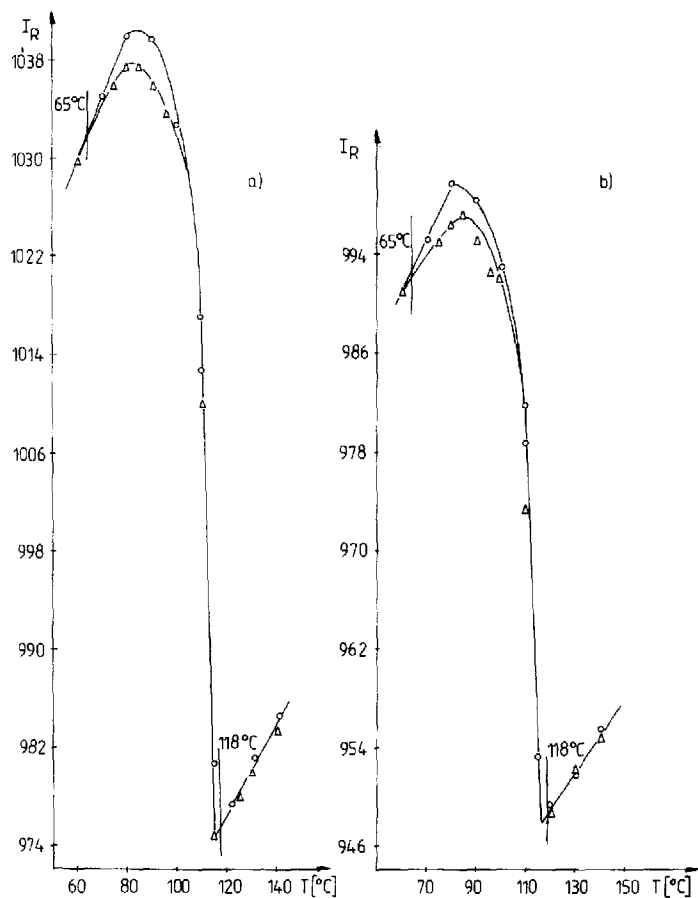


Fig. 7. Temperature dependence of the retention index of (a) *o*-xylene and (b) *m*-xylene on HPT phase deposited on Chromosorb W AW in an amount of 10%. Key as in Fig. 2.

HPT under the measuring conditions is or behaves on the support as if it were in a deeply supercooled stable state. From Fig. 6a and b we can also infer that the solubility of cyclooctane varies less in the region of the mesophase to isotropic liquid transition than that of *n*-alkanes. This indicates that *n*-alkanes dissolve more easily in the isotropic liquid than in the mesophase.

The differences in solubility also appear with xylene isomers (Fig. 7). Fig. 7a shows the temperature dependence of the retention indices of *o*-xylene and Fig. 7b those of *m*-xylene. For *o*-xylene this dependence is almost identical with that of *m*-xylene as regards the difference in the values of the retention indices in the mesophase. The difference in these values for *o*-xylene is distinctly greater, which indicates that the more compact ("more disc-like") *o*-xylene molecule reacts more strongly with the ordered disc-like molecules of the liquid crystal than do molecules with less compact (more elongated) molecules.

In Fig. 8, as in Fig. 1, we can see that the relative retentions of *p*- and *m*-xylene vary much less with temperature than those of *o*- and *m*-xylene and those of *o*- and

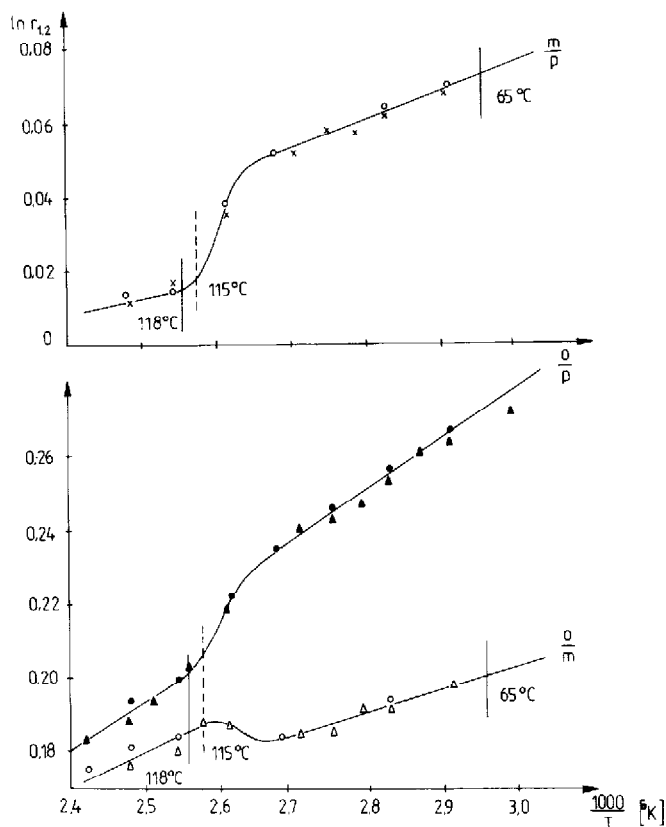


Fig. 8. Temperature dependence of the relative retention time of xylene isomers on HPT phase deposited on Chromosorb W AW in an amount of 10% during heating and cooling cycles. The dashed vertical line indicates the temperature obtained calorimetrically during cooling the liquid crystal without a support.

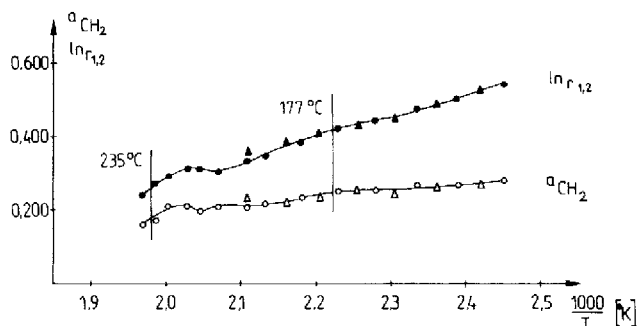


Fig. 9. Temperature dependence of the relative retention times of *cis*- and *trans*-decalin and methylene group increment on THHB phase deposited on Chromosorb W AW in an amount of 10%. Key as in Fig.

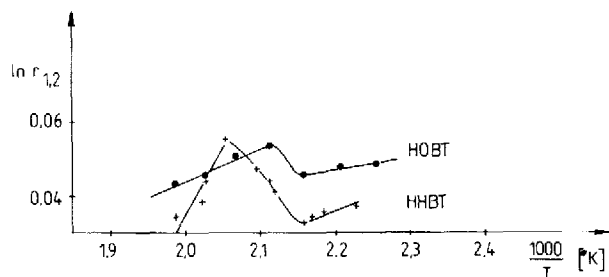


Fig. 10. Temperature dependence of the relative retention times of anthracene and phenanthrene on THHB and THOB phases deposited on Chromosorb P HMDS in an amount of 2%.

*p*-xylene. Fig. 8 also shows that there are no stepwise changes in the relative retentions at the liquid crystal melting temperature. This confirms that stable supercooling of the mesophase is possible and allows us to draw the practical conclusion that for analytical purposes one can use this stationary phase at temperatures that correspond to its solid state without the support.

Fig. 9 presents some relationships that characterize the THHB phase. From these relationships, it follows that for this phase only the temperature of the transition from the mesophase to the isotropic liquid can be determined chromatographically, but it is different from that determined calorimetrically. As with low-temperature phases, the compact decalin compounds interact more strongly with the disc-like molecules of the liquid crystal than those of *n*-alkanes.

In Fig. 10 the variation of the relative retentions of phenanthrene and anthracene is presented for columns filled with high-temperature disc-like liquid crystalline stationary phases in the cooling cycle. The maxima on the curves are related to the liquid crystal phase transition temperatures but disagree with those measured calori-

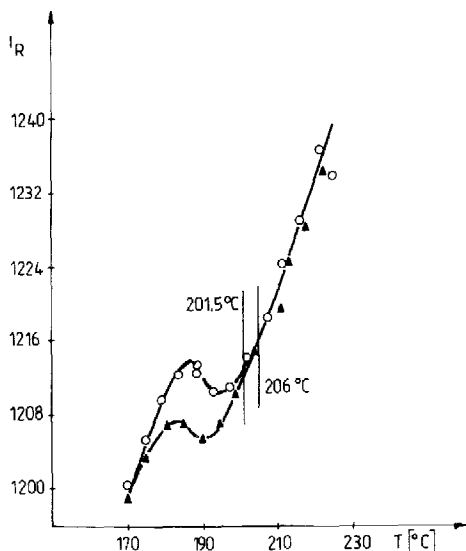


Fig. 11. Temperature dependence of the retention index on THOB phase deposited on Chromosorb W AW in an amount of 10%. Key as in Fig. 2.

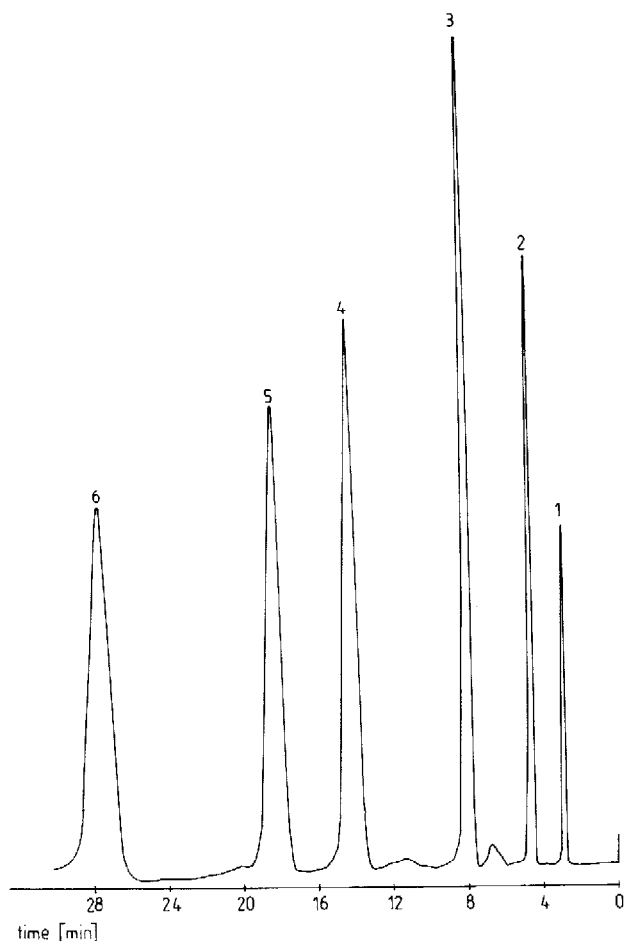


Fig. 12. Separation of a mixture on HPT phase deposited on Chromosorb W AW in an amount of 10%. (1) Heptane; (2) octane; (3) nonane; (4) *p*-xylene; (5) *o*-xylene; (6) undecane. Glass column (210 cm  $\times$  4 mm I.D.). The temperature of the column was 70°C, that of the injector 205°C and that of the detector 160°C. Argon was the carrier gas at a flow-rate of 30 cm<sup>3</sup>/min.

metrically. The relative retentions are small compared with rod-like liquid crystalline phases and one cannot expect a practically useful separation of phenanthrene and anthracene.

Fig. 11 shows the variation of the retention index of *trans*-decalin with column temperature. The hysteresis of the retention index in the temperature range of the mesophase, this temperature range being shifted towards higher temperatures compared with the range without the support, is noteworthy.

Figs. 12–14 present examples of chromatograms showing the separations of chosen mixtures. The separations are good and the peaks narrow and symmetrical. The chromatogram in Fig. 12 deserves particular attention. The boiling temperatures of the components of the mixture lie in the range 140–150°C (cyclooctane boils in the range 148–149°C and cyclooctatetraene at 142°C). Hence it is not the boiling

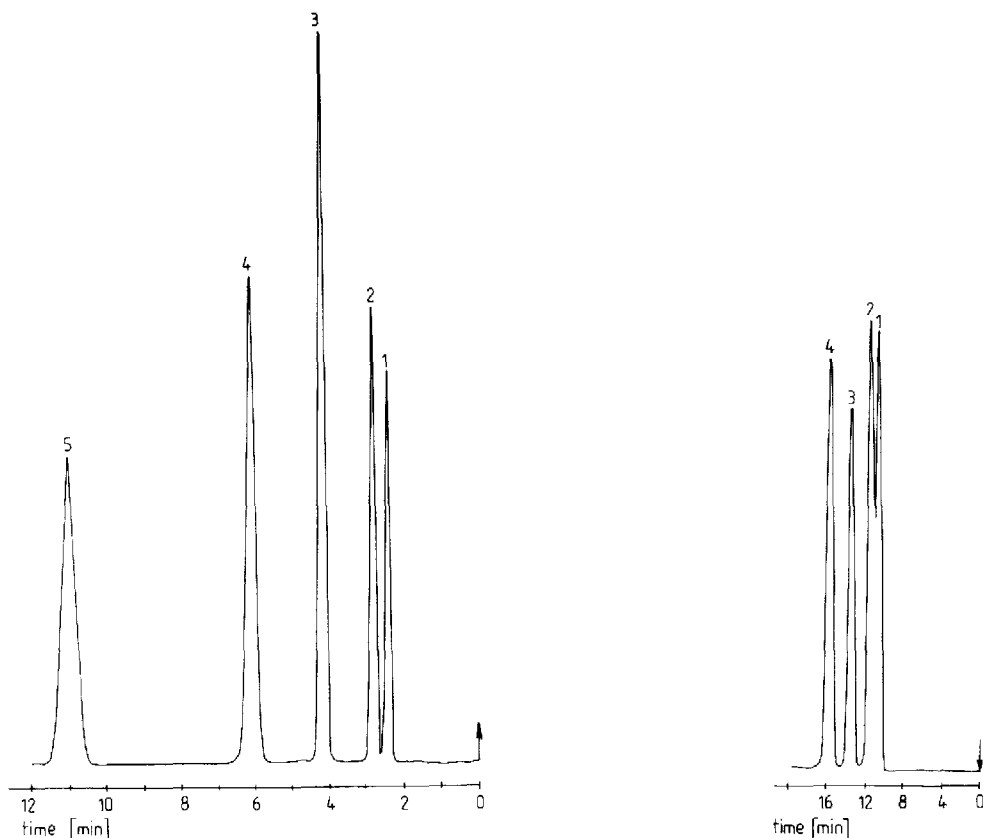


Fig. 13. Separation of a mixture on THOB phase deposited on Chromosorb W AW in an amount of 10%. (1) *trans*-Decalin; (2) *cis*-decalin; (3) tetralin; (4) naphthalene; (5) diphenyl. Glass column (210 cm  $\times$  4 mm I.D.). The temperature of column was 198°C, that of the injector 320°C and that of the detector 255°C. Argon was the carrier gas at a flow-rate of 30 cm<sup>3</sup>/min.

Fig. 14. Separation of a mixture on HPT phase deposited on Chromosorb W AW in an amount of 10%. (1) Cyclooctene; (2) cyclooctane; (3) cyclooctatetraene; (4) cyclooctadiene. Glass column (210 cm  $\times$  4 mm I.D.). The temperature of the column was 78°C, that of the injector 220°C and that of the detector 160°C. Argon was the carrier gas at a flow-rate of 30 cm<sup>3</sup>/min.

temperature but the conformation of the molecules that is decisive for the separation of these compounds on disc-like liquid crystals. This view is also supported by the fact that cyclooctane, which boils at 200°C, has a retention time almost the same as that of cyclooctatetraene.

## CONCLUSIONS

These preliminary results of tests on the properties of disc-like liquid crystalline stationary phases allow us to draw some conclusions relating to the triphenylene derivatives liquid crystals tested. It seems, however, that at least some of these conclusions will relate to other compounds from this group, because the compounds tested included triphenylene hexaalkylbenzoates, hexaalkyloxytriphenylene and

hexaalkanoatetriphenylene. It is not known, however, whether the properties of the disc-like liquid crystals from the group of benzene hexa-derivatives will be similar. They may differ, as it is for this group of compounds that large differences in the solubilities of xylene isomers have been found<sup>28</sup>, which has not found confirmation in the chromatographic properties of triphenylene derivatives. Therefore, before it will be possible to give the general properties of disc-like liquid crystalline stationary phases, further investigations must be carried out on triphenylene and especially benzene derivatives.

The results lead us to believe that the effect of the support on the properties of disc-like liquid crystalline stationary phases is greater than for other liquid crystalline stationary phases. This is confirmed by the large differences in the phase transition temperatures measured on the support and without it.

The order of elution of *p*- and *m*-xylene on disc-like liquid crystals is different from that on rod-like liquid crystals, which indicates that the separation mechanisms differ. The compounds that dissolve well in disc-like liquid crystals are those whose molecules have a compact disc-like structure. Therefore, on these phases compounds with a linear molecular structure are easily separated from those with a cyclic structure; this has been shown for the mixture of *n*-nonane and cyclooctane, which have similar boiling temperatures but very different retention times. If the molecules of the separated compounds do not have a disc-like structure, *e.g.*, *m*- and *p*-xylene, then the differences in the molecular structure are of no importance and the boiling temperature is decisive for the elution order.

The results obtained have increased our knowledge of the properties and separation mechanism of liquid crystalline stationary phases. Although preliminary, these results allow us to expect that disc-like liquid crystalline stationary phases will be of practical use in some separations.

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#### REFERENCES

- 1 A. Ono and Y. Masuda, *Chromatographia*, 17 (1983) 691.
- 2 D. G. Panse, B. V. Bapat and B. B. Ghatge, *J. Chromatogr.*, 284 (1984) 242.
- 3 J. K. Haken, *J. Chromatogr.*, 300 (1984) 1.
- 4 G. Chiavari and L. Pastorelli, *J. Chromatogr.*, 262 (1983) 175.
- 5 R. R. Heath and R. E. Doolittle, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 16.
- 6 J. F. Bocquet and C. Pommier, *J. Chromatogr.*, 261 (1983) 11.
- 7 J. E. Haky, B. Leja and H. G. Schneider, *J. Chromatogr.*, 264 (1983) 287.
- 8 D. G. Panse, S. M. Likhite, B. V. Bapat and B. B. Ghatge, *J. Chromatogr.*, 264 (1983) 279.
- 9 L. Sojak, P. Farkas and I. Ostrovsky, *Ropa Uhlie*, 25 (1983) 102.
- 10 L. Sojak, I. Ostrovsky, P. Farkas and P. Skalac, *Ropa Uhlie*, 25 (1983) 149.
- 11 Z. Witkiewicz, *J. Chromatogr.*, 251 (1982) 311.
- 12 J. Szulc and Z. Witkiewicz, *J. Chromatogr.*, 262 (1983) 141.
- 13 J. Szulc, Z. Witkiewicz and A. Ziólek, *J. Chromatogr.*, 262 (1983) 161.
- 14 Z. Witkiewicz, I. Rudnicka, J. Szulc and R. Dabrowski, *J. Chromatogr.*, 294 (1984) 127.
- 15 A. Ziólek, Z. Witkiewicz and R. Dabrowski, *J. Chromatogr.*, 294 (1984) 139.
- 16 A. Ziólek, Z. Witkiewicz and R. Dabrowski, *J. Chromatogr.*, (1984) in press.

- 17 F. Janssen, *Chromatographia*, 17 (1983) 477.
- 18 L. Sojak, P. Farkas, J. Janák, S. Rang and O. Eisen, *J. Chromatogr.*, 287 (1984) 271.
- 19 L. Zoccolillo, A. Liberti, F. Coccioli and M. Ronchetti, *J. Chromatogr.*, 288 (1984) 347.
- 20 A. Isenberg, G. Kraus and H. Zschke, *J. Chromatogr.*, 292 (1984) 67.
- 21 J. Rayss and A. Waksmundzki, *J. Chromatogr.*, 292 (1984) 207.
- 22 S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, *Pramana*, 9 (1977) 471.
- 23 Nguyen Huu Tinh, C. Destrade and H. Gasparoux, *Phys. Lett. A*, 72 (1979) 251.
- 24 Nguyen Huu Tinh, H. Gasparoux and C. Destrade, *Mol. Cryst. Liq. Cryst.*, 68 (1981) 101.
- 25 C. Destrade, M. C. Mondon and J. Malthete, *J. Phys. Colloq.*, 40 (1979) C3-17.
- 26 H. Gasparoux, *Mol. Cryst. Liq. Cryst.*, 63 (1981) 231.
- 27 C. Destrade, J. Malthete, Nguyen Huu Tinh and H. Gasparoux, *Phys. Lett. A*, 78 (1980) 82.
- 28 R. E. Goozner and M. M. Labes, *Mol. Cryst. Liq. Cryst.*, 56 (1979) 75.
- 29 J. Burwell, *Chem. Rev.*, 54 (1954) 615.
- 30 O. C. Musgrave and C. J. Webster, *J. Chem. Soc. Org.*, 8 (1971) 1393.
- 31 M. Piatelli, E. Eattorusso, R. A. Nicolaus and S. Magno, *Tetrahedron*, 21 (1965) 3229.