COMPARISON OF DIPHENYLETHANE DERIVATIVES WITH LATERAL SUBSTITUENTS AS LIQUID-CRYSTALLINE STATIONARY PHASES IN GAS CHROMATOGRAPHY

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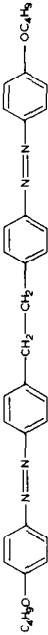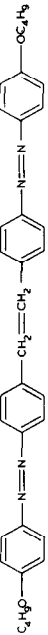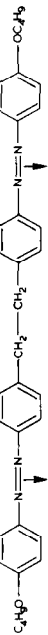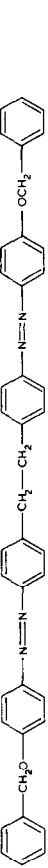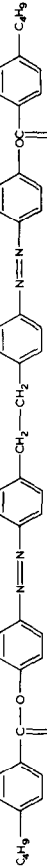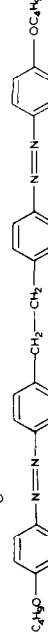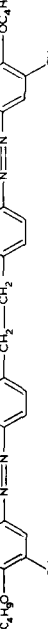(Received March 26th, 1984)

SUMMARY

The separating properties of liquid-crystalline stationary phases with the same main chain but differing in the presence or absence of lateral substituents were compared. The effect of the kind and position of the lateral substituent on the effectiveness of separation was studied. Mixtures of polynuclear aromatic hydrocarbons and isomers of naphthalene and benzene derivatives and of other compounds were separated. Some relationships were found to exist between the presence of the lateral substituents, their position in the molecule and their polarity and the effectiveness of the separation of the mixtures of various groups of compounds.
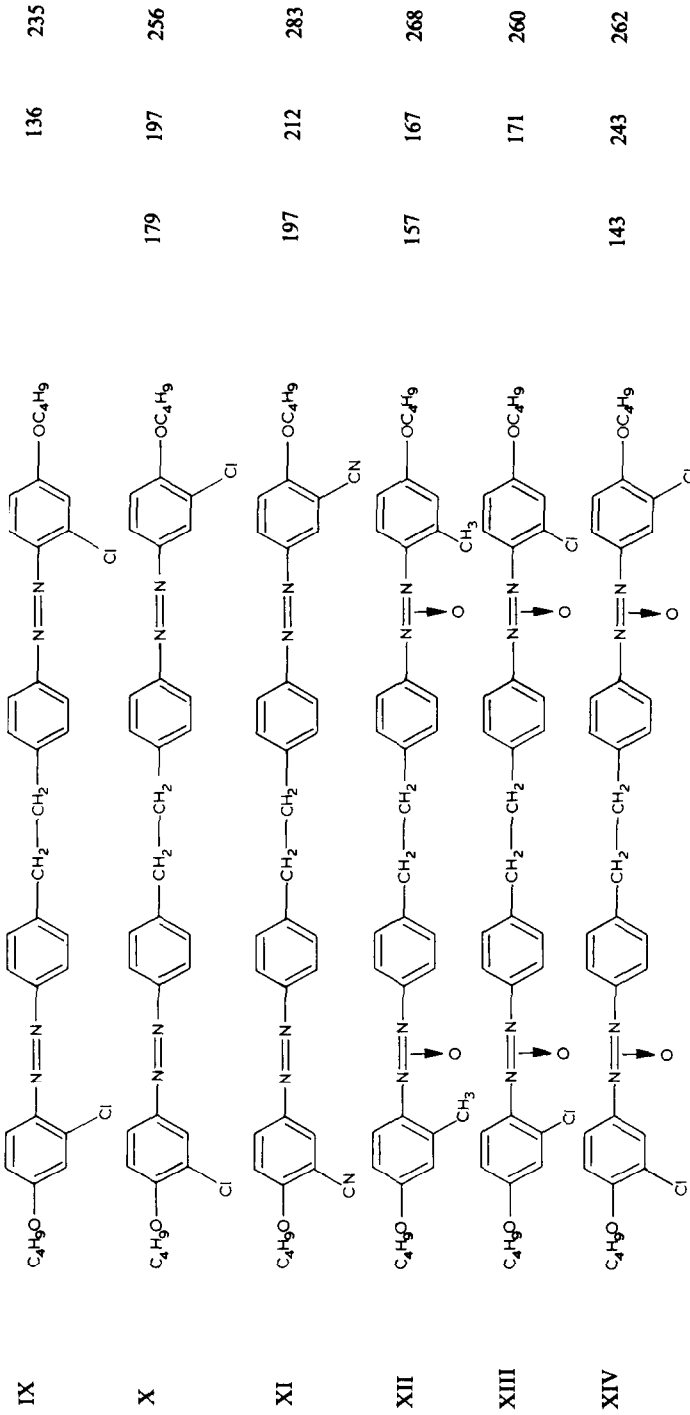
INTRODUCTION

Liquid crystals have been used successfully for separating the components of various mixtures. The synthesis of new liquid-crystalline stationary phases with wide mesophase ranges and high phase transition temperatures has made it possible to separate compounds with high boiling temperatures[1–10]. The high selectivity of liquid-crystalline stationary phases has enhanced the separation of polynuclear aromatic hydrocarbons (PAHs). The separation of PAHs presents a significant analytical problem and the use of conventional stationary phases[11–14] or of various kinds of adsorbents[15,16] has not been successful, especially when isomers were involved.

Janini and co-workers[17–20] made important achievements in separating PAHs on liquid crystals. Their results and those of others have shown that high-temperature liquid crystals can find practical application in the analysis of complex PAHs mixtures. Many problems, chiefly theoretical, involved in the analysis of PAHs on liquid-crystalline stationary phases remain, however, unsolved. The group of liquid crystals used for this purpose so far is fairly small. It is not possible, therefore, to correlate the separating properties of liquid-crystalline stationary phases with their chemical structure. Such data would allow one to plan the synthesis of new liquid-crystalline stationary phases possessing predetermined parameters. Having this in mind, we attempted to determine the relationship between the chemical structure of the liquid-crystalline molecules and their separating properties.

TABLE I

CHARACTERISTICS OF THE STATIONARY PHASES TESTED

Stationary phase No.	Formula	Temperatures of transition (°C) to phase		
		Smectic	Nematic	Isotropic
I			201	310
II		250	300	360
III		137	290	330
IV		225	250	310
V		200	229	360
VI			116 120*	229
VII			193	253
VIII			115	204

IX		136	235	
X	179	197	256	
XI	197	212	283	
XII	157	167	268	
XIII		171	260	
XIV	143	243	262	

* The compound melts at 116°C and crystallizes, yielding a form with a higher melting point.

The structures of the molecules differed in that various lateral substituents (two or four) were present or absent. The differences in the molecular structures resulting from the presence of an azo or azoxy group and the presence of various bridge-forming groups were also accounted for.

The effects of lateral substituents on the properties of liquid-crystalline stationary phases have already been examined[21–24]. However, different liquid crystals were tested that possessed fewer substituents, chiefly benzene derivatives having been separated.

The formulae and characteristics of the liquid crystals tested in this work are given in Table I. The preparative procedures and mesomorphic properties of these compounds have been described earlier[25]. They have been applied as stationary phases, and for some of them the retention parameters were measured and the selectivity and column efficiency determined[26]. In this paper we describe the results obtained when testing the separating properties of these phases towards PAHs and some benzene and naphthalene derivatives.

EXPERIMENTAL

The tests were conducted in steel columns 4 mm in diameter using a Pye Unicam GCV chromatograph with a flame-ionization detector. The column characteristics are given in Table II. Argon was used as the carrier gas, and its flow-rate was set so as to ensure the most effective separation. The temperature of the injector was established depending on the kind of substance to be separated, and that of the detector depending on the column temperature, but, always being higher than the latter. The substances to be separated were injected into the column in the form of

TABLE II

CHARACTERISTICS OF COLUMNS INVESTIGATED

Support: Chromosorb W NAW.

Column No.	Stationary phase No.	Amount of stationary phase (%)	Column length (m)
1	I	2.07	1.0
2	VII	1.98	1.0
3	X	2.12	1.0
4	XI	2.09	1.0
5	VI	2.35	1.0
6	IX	1.85	1.0
7	II	2.10	1.0
8	V*	2.08	1.0
9	III	2.22	1.0
10	IV	2.19	1.0
11	VIII	2.05	1.0
12	XII	2.30	1.0
13	XIII	2.05	1.0
14	XIV	2.05	1.0

* Support: Chromosorb W AW DMCS.

benzene solutions, their concentrations and the sizes of the samples being adjusted so as to obtain peaks of similar height. Apart from the separation of PAH mixtures prepared by combining the particular components, an extract of carbon black, obtained by burning natural gas in a heating stove, was also studied. Carbon black was extracted in a Soxhlet apparatus with methyl chloride or benzene, and the extract was concentrated.

In no instance did the tests of the separating capacity encompass the whole mesophase range. They were conducted up to a temperature at which the bleeding of the phase did not disturb the analysis.

RESULTS AND DISCUSSION

The tests on the separating properties of the liquid crystals listed in Table I allowed us to investigate the effects due to small changes in the molecular structure of the stationary phase on the separating properties. In accordance with the results presented earlier[26], phase I (with no lateral substituents) showed the highest selectivity. This phase gave also the best separation of the PAH mixture.

The chromatogram of the test PAH mixture, including benzene, phenanthrene, anthracene, fluoranthene, pyrene, terphenyl, benzophenanthrene, benzanthracene, triphenylene, chrysene, naphthacene, perylene and benzo[a]pyrene is shown in Fig. 1. The time of analysis of this mixture on a column 1 m long at 243°C was about 60 min. Increasing the column length to 1.5 m and lowering the temperature to 220°C made it possible to obtain a complete separation of all the components, but the time of analysis was then extended significantly. The order of elution of the particular
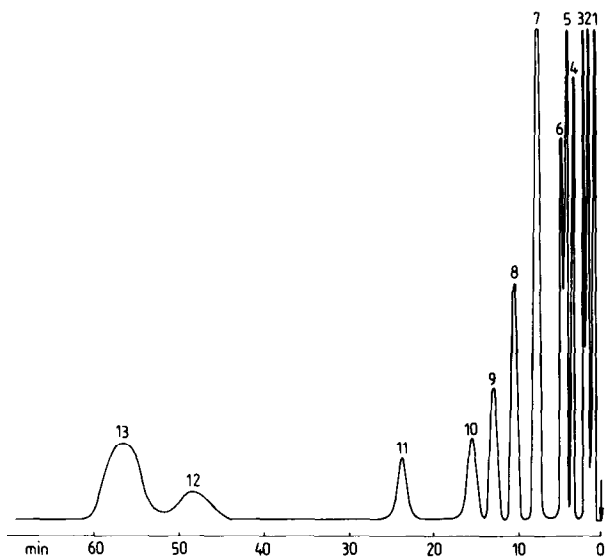

Fig. 1. Separation of a mixture containing benzene (1), phenanthrene (2), anthracene (3), fluoranthene (4), pyrene (5), p-terphenyl (6), benzo[c]phenanthrene (7), 1,2-benzanthracene (8), triphenylene (9), chrysene (10), naphthacene (11), perylene (12) and 3,4-benzo[a]pyrene (13). Column 1, column temperature 243°C, temperature of injector 320°C, temperature of detector 250°C, argon flow-rate 25 cm³/min.

Fig. 2. Separation of a mixture containing benzene (1), phenanthrene (2), anthracene (3), fluoranthene (4), pyrene (5), p-terphenyl (6), benzo[c]phenanthrene (7), 1,2-benzanthracene (8), triphenylene (9), chrysene (10), naphthacene (11), perylene (12) and 3,4-benzo[a]pyrene (13). Column 2, column temperature 230°C, temperature of injector 330°C, temperature of detector 250°C, argon flow-rate 25 cm³/min.

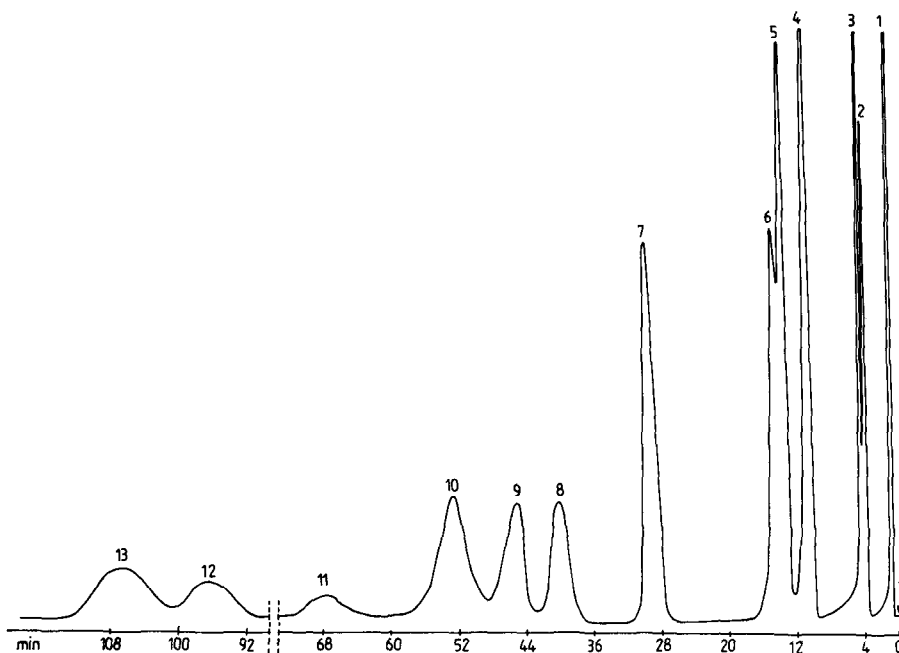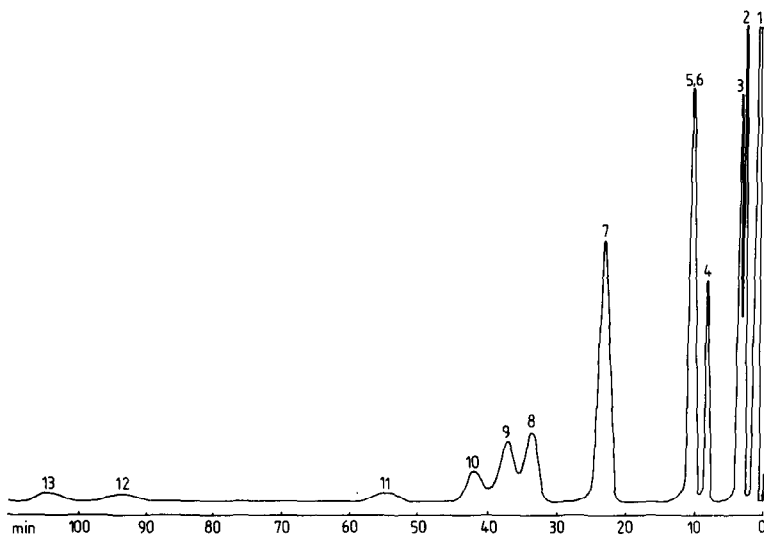Fig. 3. Separation of a mixture containing benzene (1), phenanthrene (2), anthracene (3), fluoranthene (4), pyrene (5), p-terphenyl (6), benzo[c]phenanthrene (7), 1,2-benzanthracene (8), triphenylene (9), chrysene (10), naphthacene (11), perylene (12) and 3,4-benzo[a]pyrene (13). Column 3, column temperature 230°C, temperature of injector 320°C, temperature of detector 250°C, argon flow-rate 25 cm³/min.

components was in accordance with that found by other workers. The retention time of the three-ring terphenyl included in the test mixture was longer on phase I than that of the four-ring pyrene and much longer than that of anthracene. This is due to the greater length to width ratio of the terphenyl molecule compared with anthracene and pyrene. With terphenyl, better fitting of its molecules to the ordered molecules of the liquid crystal is also possible. Thus the molecular interactions between them are also greater.

In all the cases tested the separations of PAHs on the phases with lateral substituents were worse than those on phase I, and the time of analysis was longer even when the temperature was the same. The effect of the lateral substituents on the separating properties of the stationary phases depends both on the kind of the substituent and on its position in the molecule. The elution order for phase VII (containing methyl group in the *meta*-position with respect to the azo group) is the same as for phase I (Fig. 2). The separation of pyrene and terphenyl is inferior to that obtained on phase I. On phase X, with chlorine in the *meta*-position, terphenyl was not separated from pyrene and the separation of triphenylene, benzanthracene and chrysene deteriorated (Fig. 3). Similar results were obtained on phase XI with a cyano group in the *meta*-position (Fig. 4). The order of elution of fluoranthene, terphenyl and pyrene was different than for phase I. Further, for these compounds on phase XI a significant dependence of the retention times on the column temperature was observed. At lower temperatures the relative retention time for the terphenyl–fluoranthene pair was greater than that for pyrene–terphenyl. The retention times in-
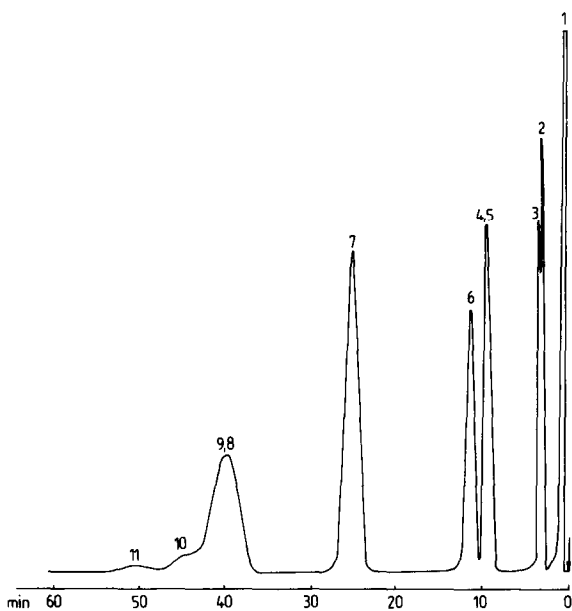

Fig. 4. Separation of a mixture containing benzene (1), phenanthrene (2), anthracene (3), fluoranthene (4), pyrene (5), *p*-terphenyl (6), benzo[*c*]phenanthrene (7), 1,2-benzanthracene (8), triphenylene (9), chrysene (10) and naphthacene (11). Column 4, column temperature 220°C, temperature of injector 320°C, temperature of detector 250°C, argon flow-rate 25 cm³/min.
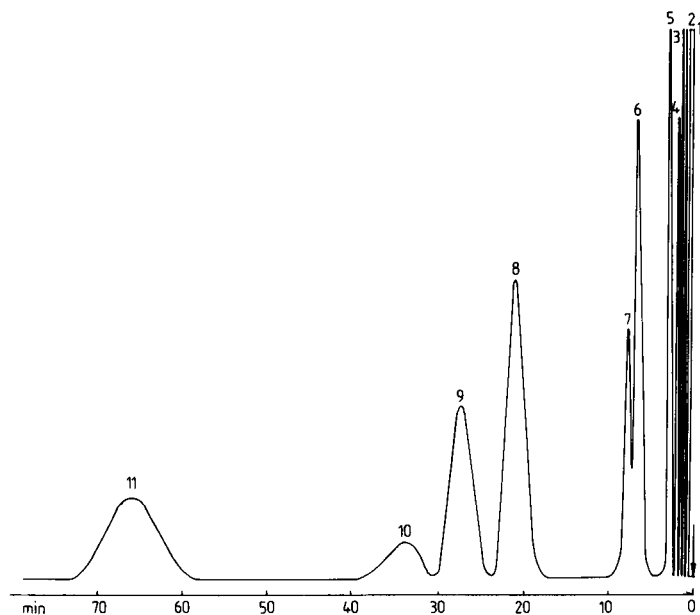
Fig. 5. Separation of a mixture containing benzene (1), naphthalene (2), biphenyl (3), acenaphthene (4), fluorene (5), phenanthrene (6), anthracene (7), fluoranthene (8), pyrene (9), *p*-terphenyl (10), and benzo[*c*]-phenanthrene (11). Column 5, column temperature 200°C, temperature of injector 300°C, temperature of detector 250°C, argon flow-rate 30 cm^3/min.

creased with temperature for the pyrene–terphenyl pair whereas for the terphenyl–fluoranthene pair they decreased.

The stationary phases with lateral substituents in the *ortho*-position with respect to the azo group could not be used at temperatures above 200°C in view of the low mesophase–isotropic liquid phase transition temperature. Above this tempera-
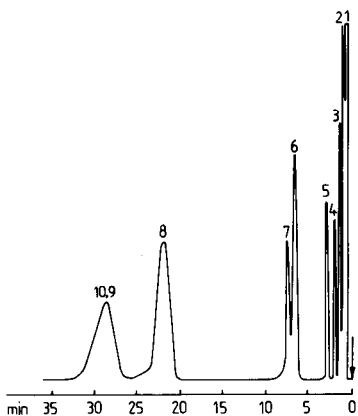

Fig. 6. Separation of a mixture containing benzene (1), naphthalene (2), biphenyl (3), acenaphthene (4), fluorene (5), phenanthrene (6), anthracene (7), fluoranthene (8), pyrene (9) and *p*-terphenyl (10). Column 6, column temperature 200°C, temperature of injector 300°C, temperature of detector 250°C, argon flow-rate 25 cm^3/min.

ture these phases were removed to a large extent from the column by the carrier gas, hence their poor usefulness in the separation of higher PAHs, as at lower temperatures hydrocarbons with larger numbers of condensed rings were retained too long in the column. In this instance the test mixture included only hydrocarbons having not more than four condensed rings in the molecule.

The separations of the tested PAHs obtained on phases VI and VIII (with methyl groups in the *ortho*-position) were similar to those obtained on phase VII (with the methyl group in the *meta*-position), although a further increase of the retention times was observed (Fig. 5). If chlorine was substituted in the *ortho*-position (compound IX), the phase ceased to have separating properties with respect to the terphenyl–pyrene pair, as was the case with the phase when chlorine was in the *meta*-position, the remaining separations being similar to those obtained on phase VI (Fig. 6).

The increased rigidity of the molecule achieved by substituting the $-CH_2-CH_2-$ bridge by the $-CH=CH-$bridge increased the melting temperature of the resultant liquid crystal (compound II). As a result, it was possible to conduct the separations of PAHs on this phase at temperatures close to that of the solid–mesophase transition, *i.e.*, under the most advantageous conditions. The resulting separations were not satisfactory, however, although the time of analysis was reduced markedly (Fig. 7). The shortening of the retention times of the chromatographed substances was much greater (the time of analysis was one third of that on phase I) than would be expected from the increase in temperature, but this was accompanied by a significant worsening of the separation. On this phase neither phenanthrene and anthracene nor perylene and benzo[*a*]pyrene were separated. The separation of tri-
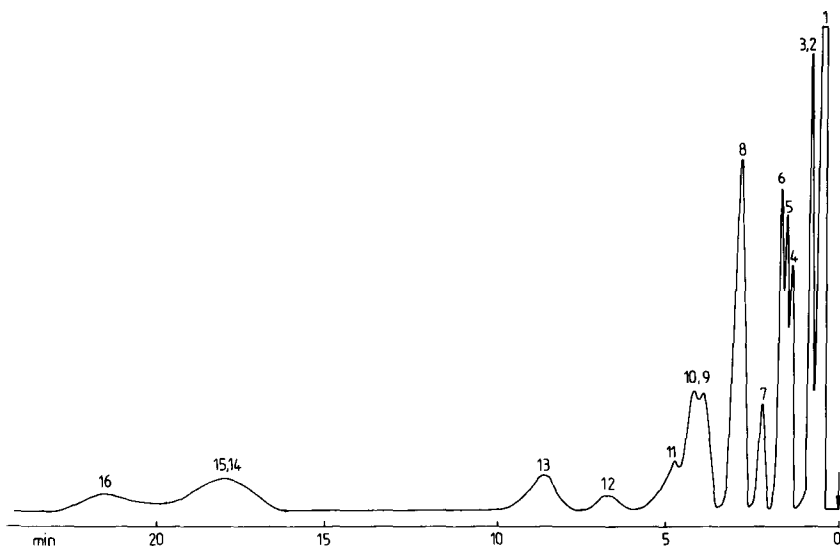

Fig. 7. Separation of a mixture containing benzene (1), phenanthrene (2), anthracene (3), *p*-terphenyl (4), fluoranthene (5), pyrene (6), benzo[*c*]phenanthrene (7), 2,3-benzofluorene (8), 1,2-benzanthracene (9), triphenylene (10), chrysene (11), naphthacene (12), 1,2-dimethylbenz[*a*]anthracene (13), perylene (14), 3,4-benzo[*a*]pyrene (15) and 20-methylcholanthrene (16). Column 7, column temperature 252°C, temperature of injector 320°C, temperature of detector 270°C, argon flow-rate 25 cm^3/min.

Fig. 8. Separation of a mixture containing benzene (1), phenanthrene (2), anthracene (3), fluoranthene (4), pyrene (5), *p*-terphenyl (6), benzo[c]phenanthrene (7), 2,3-benzofluorene (8), 1,2-benzanthracene (9), triphenylene (10) and chrysene (11). Column 8, column temperature 220°C, temperature of injector 320°C, temperature of detector 250°C, argon flow-rate 25 cm³/min.

phenylene, benzanthracene and chrysene was poor. Terphenyl was eluted before fluoranthene.

The separations of PAHs were affected negatively when the terminal substituent $-OC_4H_9$ was replaced with $-OCH_2C_6H_5$ (compound IV). The change of the butoxy for the ester group (compound V) caused an immediate improvement in the separation of PAHs, especially for lower boiling compounds. However, at the same
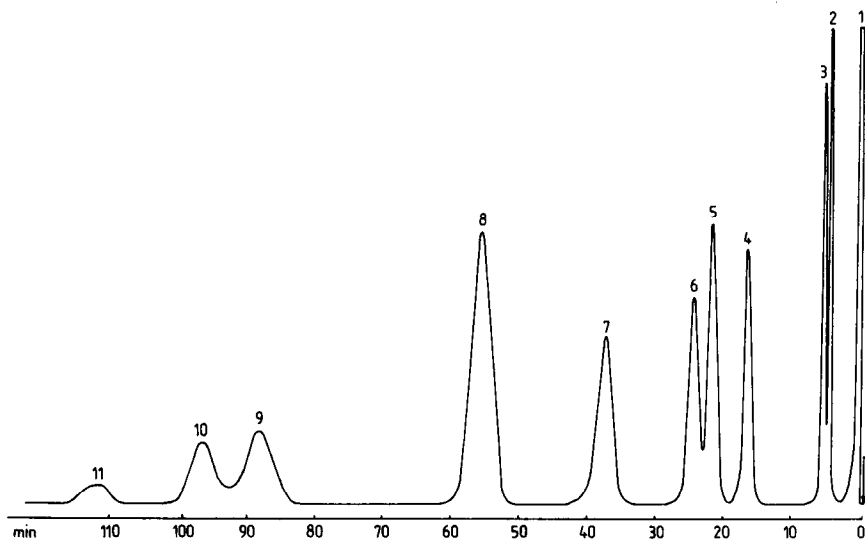

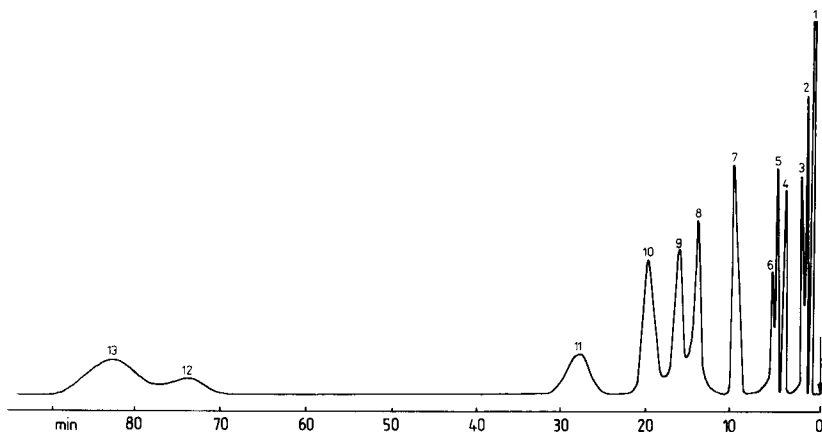Fig. 9. Separation of a mixture containing benzene (1), phenanthrene (2), anthracene (3), fluoranthene (4), pyrene (5), *p*-terphenyl (6), benzo[c]phenanthrene (7), 1,2-benzanthracene (8), triphenylene (9), chrysene (10), naphthacene (11), perylene (12) and 3,4-benzo[a]pyrene (13). Column 9, column temperature 215°C, temperature of injector 320°C, temperature of detector 250°C, argon flow-rate 30 cm³/min.

time we observed an increase in the retention times of the chromatographed sub-
stances. The order of elution of the particular components of the mixture was the
same as for phase I (Fig. 8).

Oxidation of the azo to azoxy compounds adversely affected the separation
properties of the tested phases with regard to PAHs. The retention times of lower
boiling substances were reduced on phase III (Fig. 9) compared with phase I, the
retention times of higher boiling compounds being increased. The peaks broadened
even when the absolute retention times changed only very slightly. Thus the sepa-
rations were worse than for the azo compounds.

Different results were obtained when we tested the separation efficiency with
regard to naphthylamine isomers. The 1- and 2-naphtylamines did not separate on
phases I, II and IV (with no lateral substituents). The separation efficiency on phases
with lateral substituents depended, as for PAHs, on the kind and position of the
substituent. The best separation of naphthylamine isomers was obtained on phase
XI, possessing a cyano group in the *meta*-position (Fig. 10). If the liquid crystal
molecule had a chlorine atom instead of the cyano group (phase X), the separation

Fig. 10. Separation of a mixture containing benzene (1), 1-naphthylamine (2) and 2-naphthylamine (3).
Column 4, column temperature 180°C, temperature of injector 300°C, temperature of detector 200°C,
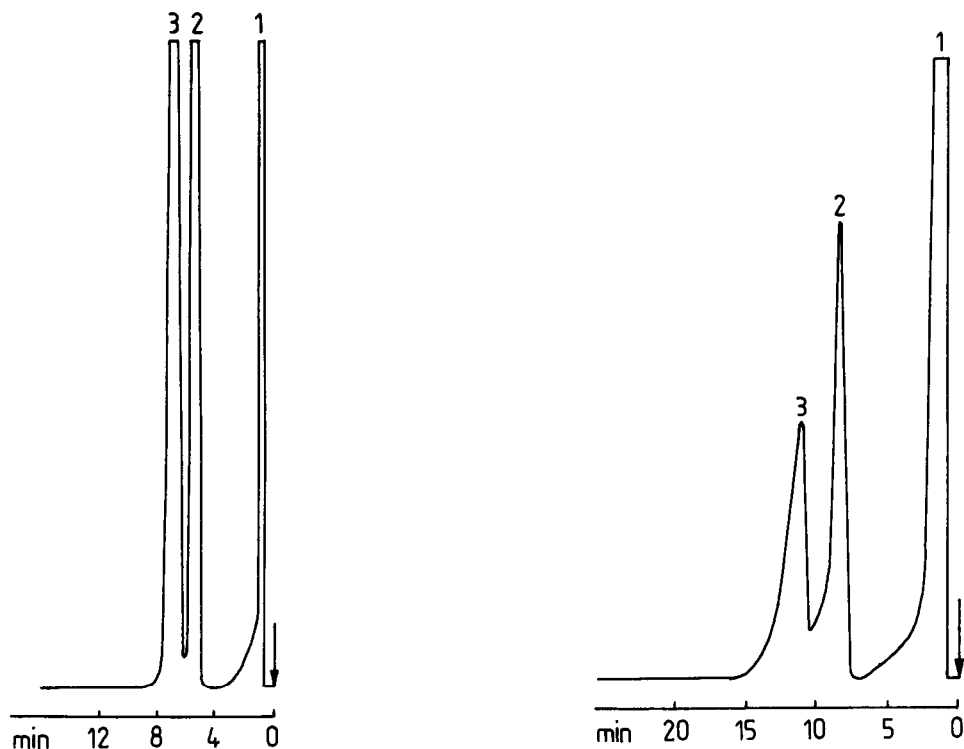argon flow-rate 25 cm³/min.

Fig. 11. Separation of a mixture containing benzene (1), 1-naphthylamine (2) and 2-naphthylamine (3).
Column 5, column temperature 170°C, temperature of injector 300°C, temperature of detector 200°C,
argon flow-rate 30 cm³/min.

was almost identical, but if the methyl group was present, broadening of the peaks is observed (Fig. 11). The effect of the polarity of the chromatographed molecule was marked here. The effect of the position of the substituent was less drastic in the separation of naphthylamine isomers than when PAHs were involved. The naphthylamine isomers were separated on all the phases that had azoxy groups in their molecules. The relative retention times of 1- and 2-naphthylamines were greater on these phases than on the relevant phases with an azo group. However, as the increase in the absolute retention times was accompanied by broadening of the peaks, the separations were less effective.

The presence of lateral substituents in the stationary phase molecule, as with naphthylamines, favoured the separation of other naphthalene and benzene derivatives. In this instance the position of the substituent was crucial. The separation of 1- and 2-bromonaphthalenes and 1- and 2-ethylnaphthalenes was carried out on phases VI, VIII and IX with lateral substituents in the *ortho*-position with respect to the azo group (Figs. 12 and 13). These separations took place neither on the phases with the same substituents in the *meta*-position nor on the phases with an azoxy group in the molecule.

A partial separation of the isomers of methyl derivatives of naphthalene was obtained on liquid crystals with lateral substituents in the *ortho*-position. The separations were, however, not completely satisfactory although better than those on the other phases tested.

It is interesting that 2-methylnaphthalene was retained longer than 1-methylnaphthalene on phases VI and VIII with the methyl group in the *ortho*-position. On all the remaining phases the elution order was reversed, which is in agreement with the boiling temperatures.

We also succeeded in separating on the phases tested 1- and 2-naphthols, *o-*, *m-* and *p*-chloroanilines, *o-*, *m-* and *p*-toluonitriles and mixtures of compounds differing in the sizes of the molecules, *e.g.*, mixtures of phthalates and mixtures of *p*-cyanobenzoic esters. The phases tested were used successfully for determining the purity of many compounds, chiefly liquid crystals with low melting points and of the products used for their synthesis.

We carried out the analysis of an extract of carbon black from a gas furnace (Fig. 14) on phase I. The chromatogram obtained showed 28 peaks but the components of the mixture were not identified.

From the analysis of the results, one can draw conclusions about the effect of changes in the molecular structure of a liquid crystal on its separating properties. The best separating properties with respect to PAHs were shown by phase I. The structure of the nematic phase of compound I allows the penetration of the large PAH molecules. The specific interactions between the solvent and the solute are sufficiently strong to allow separation. The sufficiently high relative retention times together with the not very long absolute retention times ensure an effective separation of the tested PAH mixture on phase I.

The rigid and flat structure of compound II makes possible a more compact arrangement of the molecules in layers. This compound is a smectic so the penetration of the solute into the highly ordered layers of its molecules is hindered. The dissolution of the PAH molecules probably proceeds in the interlayer spaces where the specific interactions between the stationary phase and solute molecules are weaker.
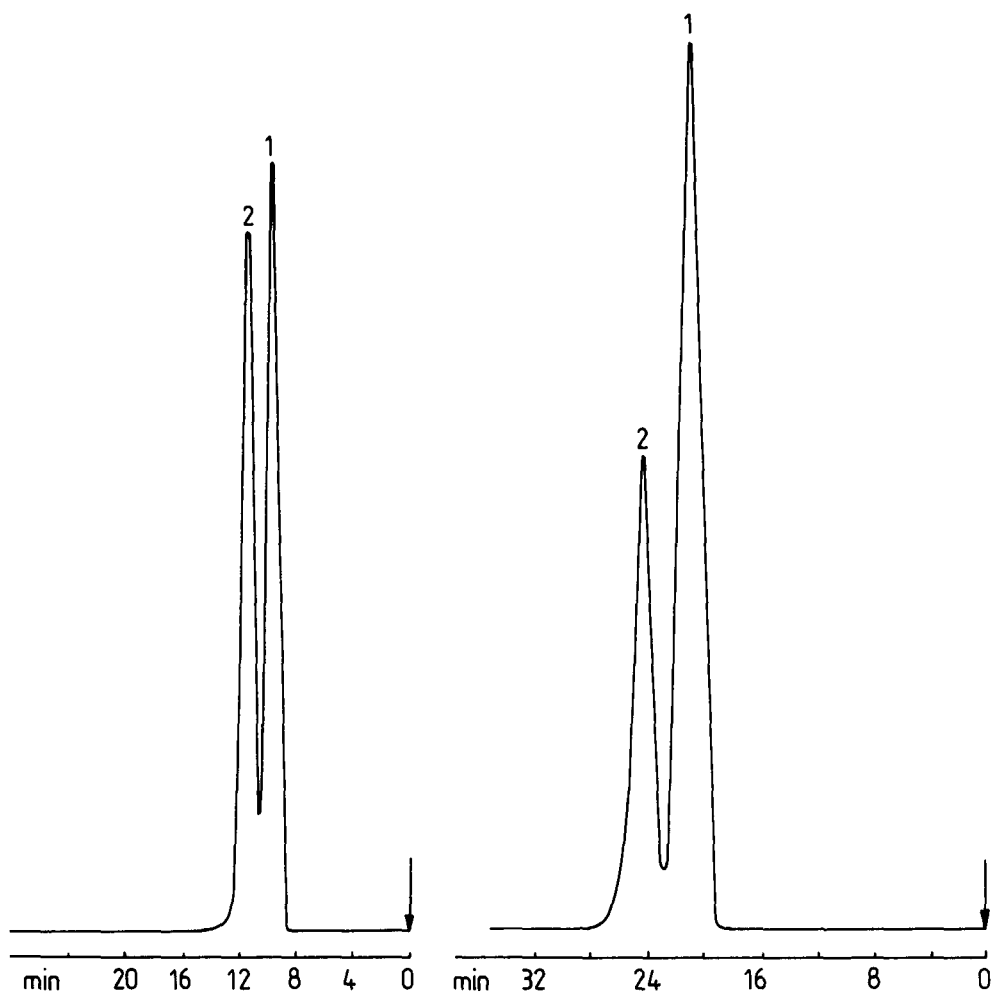
Fig. 12. Separation of a mixture containing 1-ethylnaphthalene (1) and 2-ethylnaphthalene (2). Column 11, column temperature 120°C, temperature of injector 280°C, temperature of detector 180°C, argon flow-rate 25 cm³/min.

Fig. 13. Separation of a mixture containing 1-bromonaphthalene (1) and 2-bromonaphthalene (2). Column 11, column temperature 120°C, temperature of injector 280°C, temperature of detector 180°C, argon flow-rate 25 cm³/min.

We observe on this phase a decrease in the absolute retention times but at the same time a significant lowering of the relative retention times compared with phase I. This has an adverse effect on the separation of PAHs. Compounds III and V, which also yield smectic phases, do not differ significantly from phase I as regards their separation properties with respect to PAHs, as in view of the very flexible structure of their molecules they cannot be as densely packed as compound II in the mesophase. Compounds III and V are probably smectics of low ordering, and therefore reveal
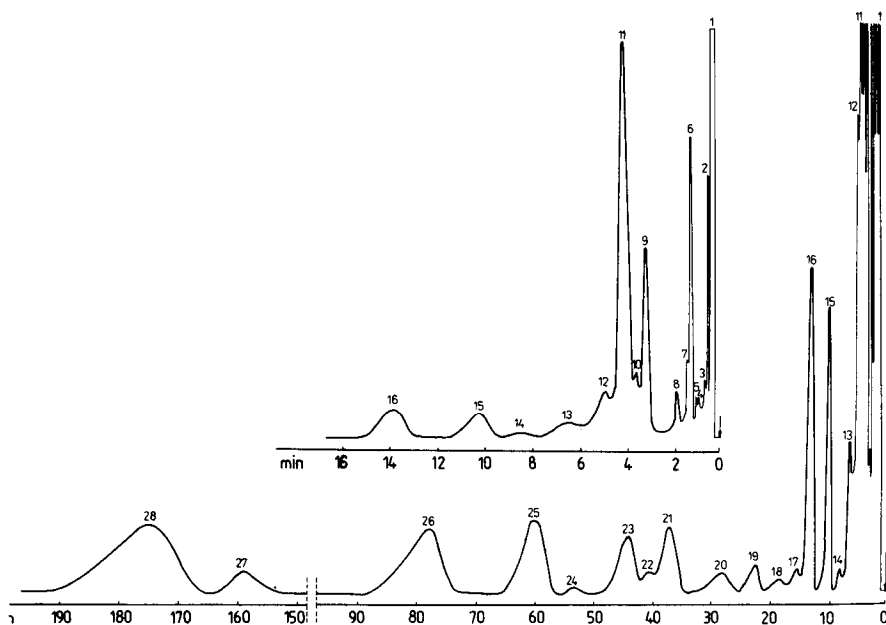
Fig. 14. Separation of a benzene extract of carbon black. Column 1, column temperature 237°C, temperature of injector 330°C, temperature of detector 260°C, argon flow-rate 25 cm³/min.

separating properties similar to those of nematics. The introduction of lateral substituents widens the molecules, reduces the regularity of their shape and increases the intermolecular distances in the mesophase. This is probably why the intermolecular reactions in the liquid crystal become weaker. As a result, penetration of the PAH molecules into the mesophase structure is facilitated and their solubility increases. The greater solubility of the PAH molecules contributes to the increase in the absolute retention times of the chromatographed substances on the stationary phases whose molecules have lateral substituents. The increase in the relative retention times simultaneously observed in some instances is due to the increased specific interactions of the phase with the solute. The increase in the absolute retention times with respect to phase I is greater on phases with lateral substituents in the *ortho*-position than on phases with the same substituents in the *meta*-position. The phases with lateral substituents reveal a significant specific separating activity that depends not only on the position of the substituent but also on its type. The effect of the type of substituent is related to its polarity. The influence of the polarity of the stationary phases is observed when analysing the separating properties of the tested phases with respect to naphthylamines, although it cannot be neglected in the separation of PAHs.

The effects of the position and type of substituent on the separating properties of stationary phases cannot be considered in isolation from the type of molecules of the compounds being separated. It is known that non-polar compounds are better separated on non-polar phases, the effect of the position of the lateral substituent in the liquid-crystalline stationary phase then being significant. When polar compounds are chromatographed, their separation depends more on the polarity than on the position of the substituent.

CONCLUSIONS

The liquid-crystalline phases tested are suitable for separating many groups of high-melting compounds and also polynuclear aromatic hydrocarbons. The fairly long analysis times of higher PAHs could be reduced by using capillary columns. The results obtained in the course of these investigations allow us to conclude that a strict relationship exists between the chemical and geometric structures of the liquid-crystalline phases tested and their separating properties.

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