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INVESTIGATIONS OF THE PROPERTIES OF LIQUID-CRYSTALLINE STATIONARY PHASES CONTAINING NAPHTHALENE FRAGMENTS IN THEIR MOLECULES

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SUMMARY

Six new liquid-crystalline stationary phases have been produced containing naphthalene fragments in their molecules. The mesophase range lies between 45 and 132°C, the highest clearing temperature being 295°C and the lowest melting point 126°C. The physicochemical properties of these stationary phases have been tested, and the usefulness of the phases for the analysis of polycyclic aromatic hydrocarbons, naphthylamines, naphthols and methylnaphthalene isomers has been demonstrated.

INTRODUCTION

Liquid-crystalline phases are of considerable interest, recent studies¹⁻¹² being devoted to the synthesis of new stationary phases and to investigations of their physico-chemical and analytical properties. Similar investigations have been conducted in our laboratory¹³⁻¹⁶. At present we are concentrating on the synthesis and testing of liquid-crystalline stationary phases containing a naphthalene fragment in the molecule. Previous work¹⁷⁻¹⁹ has shown that such phases exhibit better separation properties with respect to isomers of naphthalene derivatives than those which do not contain naphthalene fragments.

One of the phases investigated did not reveal liquid-crystalline properties. However, its properties were also studied for the sake of comparison with the others.

SYNTHESIS OF THE LIQUID-CRYSTALLINE STATIONARY PHASES

The products are obtained in two steps. First 4-substituted aniline is diazotized and coupled with 1-naphthol or phenol. Then the resulting hydroxyazo compound is converted into the ester by reaction with an organic acid chloride.

The characteristics of the new liquid-crystalline nematic stationary phases are given in Table I. Their preparation is typified by that of phase II, *i.e.*, 4-(4'-*n*-butylbenzoyloxy)naphthalene-1-azo-(4'-methoxybenzene).

4-Hydroxynaphthalene-1-azo(4'-methoxybenzene) (first step)

A solution of *p*-anisidine hydrochloride was prepared in a 1000-cm³ beaker from 73.8 g (0.6 mole) *p*-anisidine, 136 cm³ concentrated hydrochloric acid and 374 cm³ water. The solution was cooled to 0–5°C when 45.5 g (0.66 mole) sodium nitrite in 100 cm³ water were added dropwise with vigorous stirring. Separately, 90.7 g (0.63 mole) of 1-naphthol were dissolved in a 4000-cm³ beaker in a solution obtained from 64.8 g (1.62 mole) of sodium hydroxide and 1500 cm³ water. After complete dissolution and cooling to 10°C, the diazotized *p*-anisidine was then added portionwise. The reaction mixture was agitated for 2 h and subsequently acidified with hydrochloric acid to pH < 7. The hydroxyazo compound which precipitated was filtered off and recrystallized from methanol, yield 100 g (60%), m.p. 164–166°C. The procedure described differs from that of Charrier and Casale²⁰ who obtained a product of m.p. 168°C.

The crude 4-*n*-butyl-4'-hydroxyazobenzene (semiproduct for phase I) also obtained in this way was purified by heating three times in boiling *n*-hexane and filtering. The yield was 69% and the m.p. 80°C (Lit.²¹, m.p. 81°C).

In the case of 4-hydroxynaphthalene-1-azo-(4'-hydroxybenzene), the semiproduct for phase VII, 4-aminophenol was diazotized analogously and the coupling with 1-naphthol was carried out in a sodium hydroxide solution whose volume was 1.5 times greater than in the procedure detailed above.

In the second reaction step the crude product from the first step was used.

4-(4''-Butylbenzoyloxy)naphthalene-1-azo-(4'-methoxybenzene) (second step)

In this step 24 g (0.086 mole) of 4-hydroxynaphthalene-1-azo-(4'-methoxybenzene) were placed in a three-neck flask (1500 cm³) together with 13 g (0.172 mole) of pyridine and 700 cm³ of benzene. To this mixture were added dropwise 17 g (0.086 mole) of 4-*n*-butylbenzoylchloride whereupon the temperature rose by about 5°C. After all the chloride had been introduced, the contents of the flask were heated to 50–60°C for 2 h and the flask left to stand overnight at ambient temperature. The next day the mixture was poured into water acidified with hydrochloric acid and 500 cm³ benzene were added. The mixture was shaken and the benzene layer was separated, dried with anhydrous magnesium sulphate and filtered through silica gel. The benzene was then distilled off and the residue recrystallized thrice from an ethanol–acetone (2:1) mixture. The product obtained melts at 126–127°C and its clearing temperature is 195°C.

The remaining liquid-crystalline stationary phases were obtained in the same way, with the only difference being that in the cases of phases V and VII the esterification was conducted in chloroform and not in benzene. Phase I was recrystallized once from ethanol and then from *n*-hexane, phase V was extracted with acetone in a Soxhlet apparatus and phase VI was recrystallized twice from acetone.

THE PHYSICO-CHEMICAL PROPERTIES OF THE LIQUID-CRYSTALLINE STATIONARY PHASES

The stationary phases were deposited on Chromosorb W AW DMCS in amounts of 10% (w/w) from a methylene chloride solution, the solvent being evaporated in a rotary vacuum evaporator. The packing was then dried and screened; the

TABLE I
CHARACTERISTICS OF THE NEW STATIONARY PHASES

Phase notation	Formula	Mesophase range (°C)
I		m.p. 107 (nc mesophase)
II		126-195
III		131-204
IV		202-247
V		177-295
VI		167-212
VII		143-275

0.15–0.20 mm fraction was used in the experiments. The investigations were carried out on a Pye Unicam Type GCV gas chromatograph with a flame ionization detector. The temperature of the injector was 240°C and that of the detector 190°C. The packed columns were heated for 2 h at 180°C before use.

Most stationary phases were tested in the range 110–170°C, so that at the lower temperatures the columns operated under supercooled mesophase conditions. The results were the same irrespective of whether the temperature chosen was reached by heating or cooling. By use of the thermo-optical method it was found that the phases had a strong tendency to become supercooled, even at ambient temperature. This was not true, however, of phases III and IV. In the case of phase IV, which has a high melting point, no results could be obtained in the temperature range 110–170°C by the measuring procedure used.

Selectivity tests were carried out using a mixture of nonane, decane and undecane, and a mixture of diethylbenzene isomers.

A portion ($5 \times 10^{-5} \text{ cm}^3$) of each mixture was introduced into the column. In a single experiment it was possible to calculate from the measured retention times the dead time, the retention indexes and relative retention times for diethylbenzenes at a given column temperature. When the separation of diethylbenzenes was not satisfactory, a mixture containing the alkanes and a single diethylbenzene isomer, or two isomers that are well separated under the column conditions, was used.

The dead time, t_d , was found from the formula²²

$$t_d = \frac{t_n t_{n+2} - t_{n+1}^2}{t_n + t_{n+2} - 2t_{n+1}}$$

where t_n , t_{n-1} and t_{n-2} are the retention times of successive members of the alkane homologous series.

The retention indexes (J) for diethylbenzenes were found from the formula²²

$$J = 190 \cdot \frac{\ln(t_R - t_d) - \ln(t_{11} - t_d)}{\ln(t_{11} - t_d) - \ln(t_{10} - t_d)} + 1100$$

where t_R , t_{11} and t_{10} are the retention times of one of the diethylbenzene isomers, undecane and decane, respectively. The values obtained are presented in Fig. 1.

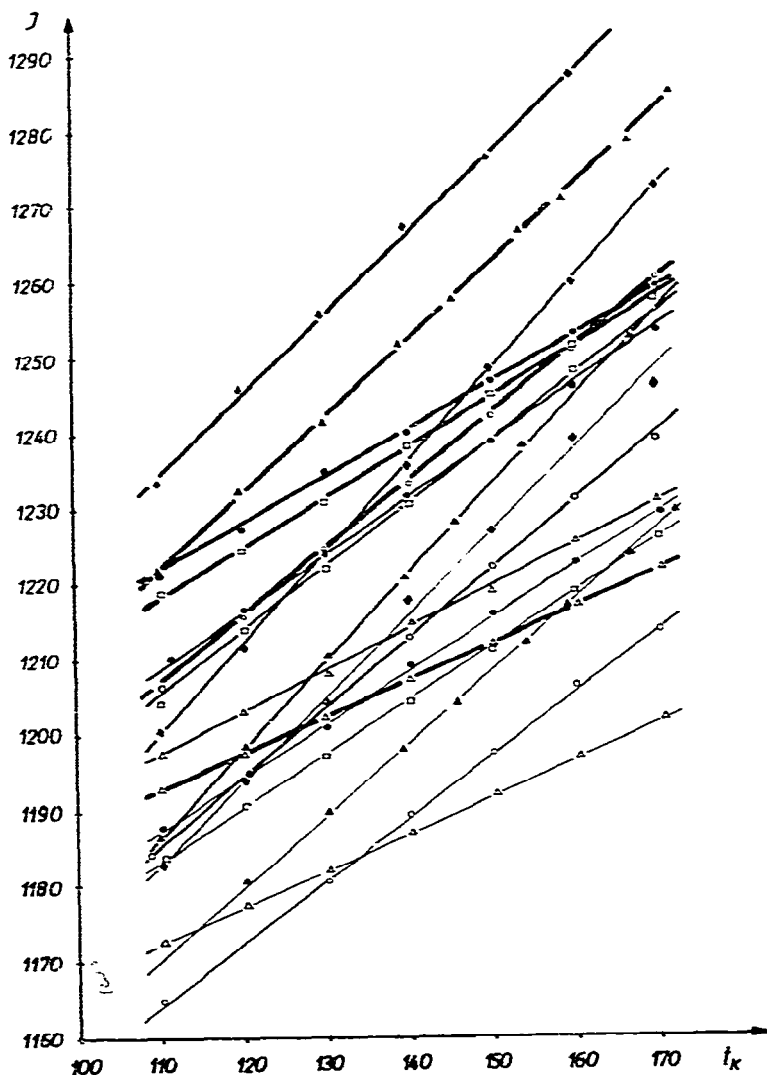


Fig. 1. Retention indexes of *para* (—), *ortho* (—) and *meta* (—) diethylbenzenes on the phases I (Δ), II (\square), III (\bullet), V (\blacktriangle), VI (\blacklozenge) and VII (\circ).

The diethylbenzene retention indexes measured on the present stationary phases are directly dependent on temperature, according to the relation:

$$I = at + b$$

The values of the coefficients a and b were calculated by the least squares method and are summarized in Table II. The temperature dependence of the retention index of *o*-diethylbenzene is the most pronounced on the liquid-crystalline phases, in contrast to the behaviour of that isomer on the isotropic phase I where its retention index shows the weakest temperature dependence. The temperature dependence of all diethylbenzene isomers is higher on liquid-crystalline phases than on the isotropic one.

When testing liquid-crystalline stationary phases, considerable attention is usually paid to the interactions of the liquid crystals with poorly separable *meta*- and *para*-isomers, and eventually to the differences between those interactions. Therefore we also decided to determine how the difference of the retention indexes of the *meta*- and *para*-isomers varies within the mesophase range of the tested compounds. If the retention indexes are linear functions of temperature, then their differences will also depend linearly on temperature. The variation of that difference is, however, small because of the similar values of coefficient a for the *meta*- and *para*-isomers.

For the isotropic phase the difference between the retention indexes of *p*- and *m*-diethylbenzene amounts to about 20 units in the temperature range 100–200°C. For liquid-crystalline phases the difference is much greater, and increases with increasing selectivity of the stationary phase; for phase V it exceeds 50 units. It was found that, in the given temperature range, the more selective the liquid-crystalline stationary phase is, compared with other phases, the higher is its clearing point.

The difference between the retention indexes of *p*- and *m*-diethylbenzenes on liquid-crystalline phases decreases with increasing temperature, whereas it increases on the isotropic phase.

The polarity of the stationary phases was determined by a method proposed by Rohrschneider²³ and McReynolds²⁴.

Recently the method of determining polarity on the basis of the retention indexes has been extended to include liquid-crystalline stationary phases. Addition-

TABLE II

VALUES OF THE COEFFICIENTS a AND b GIVEN BY THE FORMULA $I = at + b$ FOR DIETHYLBENZENE ISOMERS

Phase	<i>meta</i>		<i>ortho</i>		<i>para</i>	
	a_m	b_m	a_o	b_o	a_p	b_p
I	0.529	1108	0.604	1124	0.561	1123
II	0.715	1100	0.837	1108	0.680	1138
III	0.679	1106	0.804	1114	0.652	1144
V	0.950	1066	1.150	1061	1.020	1110
VI	1.118	1056	1.205	1064	1.073	1112
VII	0.843	1067	0.927	1079	0.895	1105

TABLE III

DIFFERENCES BETWEEN THE RETENTION INDEXES OF THE TEST SUBSTANCES AS MEASURED ON THE LIQUID-CRYSTALLINE STATIONARY PHASES AND ON SQUALANE

Stationary phase	Difference					
	<i>x</i>	<i>y</i>	<i>z</i>	<i>u</i>	<i>s</i>	<i>g</i>
I	124	208	205	285	236	0
II	171	256	244	340	296	11
V	177	250	236	329	303	25
VI	195	309	274	388	337	17
VII	166	245	220	318	287	19
Difference between the highest and lowest values	71	101	69	103	101	25

ally, the difference between the *p*- and *m*-xylene retention indexes at 120°C, obtained on a given liquid-crystalline phase, has been introduced²⁵. This method has a disadvantage in that the selectivity of the liquid-crystalline stationary phase that affects the difference of the retention indexes depends largely on the value of the clearing point and the related mesophase range. Despite that, we decided to use the method in order to allow comparison of our liquid-crystalline phases with those investigated by other authors.

The retention indexes, I_x , of the test substances were found from the retention times of the alkanes, $t_{R,z}$ and $t_{R,z+1}$, and those of the test substances, $t_{R,x}$, using the formula:

$$I_x = 100 \cdot \frac{\ln(t_{R,x} - t_d) - \ln(t_{R,z} - t_d)}{\ln(t_{R,z+1} - t_d) - \ln(t_{R,z} - t_d)} + 100 =$$

The dead time, t_d , was found as described previously.

The test substances were introduced successively into the column at 120°C in volumes of 10^{-2} cm³ each. The alkanes were introduced into the column in the form of a mixture containing all the alkanes from heptane to undecane, also in portions of 10^{-2} cm³.

The calculated differences between the retention indexes of the test substances on the present stationary phases and on squalane are summarized in Table III. For squalane we assumed the following values of the retention indexes: benzene, 671; butanol, 599; pentanone, 632; nitropropane, 667; pyridine, 736²⁶. The calculated values are denoted by the letters *x*, *y*, *z*, *u* and *s*. The letter *g* denotes the difference between the retention indexes of *p*- and *m*-xylene on the tested stationary phase.

It follows from the values obtained that all the tested stationary phases exhibit low polarities. If we compare the data in the table with the retention indexes for diethylbenzenes, we see that the sum of the retention indexes for diethylbenzene isomers increases with increasing value of *x*, which characterizes the interaction of the

given phase with the benzene ring: I (3599) < VII (3645) < II (3681) < III (3687) < V (3711) < VI (3736).

The direction of retention index variations of different test substances, used to test one phase, is similar, *i.e.* an increase in retention index of one substance is related to the increase in retention index of another substance.

The tested stationary phases differ little as regards their interaction with the benzene ring (dispersive interaction) and their orientational interaction. The greatest differences between the particular phases lie in their ability to bind and split off a

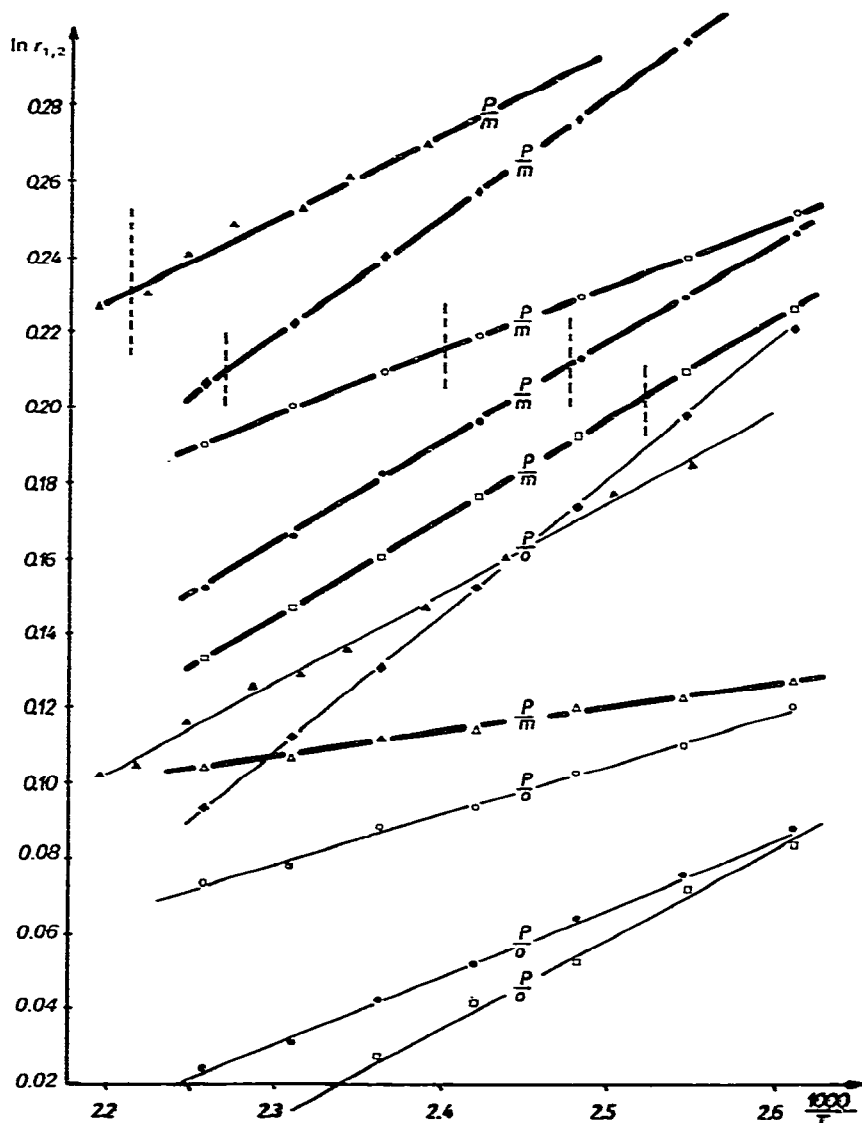


Fig. 2. Relative retention times of *p*- and *m*- and *p*- and *o*-diethylbenzenes. Key as in Fig. 1. The dashed lines represent the melting points of the stationary phases.

proton, which is connected with dipole-orientational interactions and the interaction with free electron pairs. A high capacity for dipole-orientational interactions is a common feature of all the tested stationary phases. There is a direct relation between the polarity of a given phase and the chemical structure of its molecule.

The selectivity of the studied stationary phases has been expressed as the relative retention time of the diethylbenzene isomers

$$r_{1,2} = \frac{t_{R1} - t_d}{t_{R2} - t_d}$$

where t_{R1} and t_{R2} are the retention times of the diethylbenzene isomers and t_d is the dead time. The results are presented in Fig. 2. The highest selectivity towards *p*- and *m*-diethylbenzene is exhibited by phase V. The temperature dependence of the selectivity is strongest for phase VI, and is related to the large difference in the dissolution enthalpies of the isomers in that phase. The selectivity of phase VII shows the smallest temperature dependence; this phase is characterized by a wide temperature range of the mesophase.

The dissolution enthalpies of *p*-diethylbenzene in the mesophase were calculated from:

$$\ln k = \Delta H/RT + C$$

where $k = (t_R - t_d)/t_d$. The slope, $\Delta H/R$, of the variation of $\ln k$ with the reciprocal of temperature was calculated by the least squares method from at least nine measurements in the range 100–170°C.

Similarly, we used the relation

$$\ln \frac{t_{R1} - t_d}{t_{R2} - t_d} = \frac{-\Delta H_1 + \Delta H_2}{RT} + \frac{\Delta S_1 - \Delta S_2}{R}$$

to calculate the differences in the standard enthalpy and entropy of dissolution of diethylbenzene isomers making use of the relations:

$$-\Delta H_1 + \Delta H_2 = AR$$

and

$$\Delta S_1 - \Delta S_2 = BR$$

The coefficients in the equation

$$\ln \frac{t_{R1} - t_d}{t_{R2} - t_d} = A \cdot \frac{1}{T} + B$$

were found, as above, by the least squares method. In both cases the correlation coefficient was not less than 0.999. The results are summarized in Table IV.

The absolute value of the dissolution enthalpy for *p*-diethylbenzene is less than that of the condensation enthalpy (−44.8 kJ/mole) for all stationary phases, being

TABLE IV

DISSOLUTION ENTHALPIES AND THE DIFFERENCES BETWEEN DISSOLUTION ENTHALPIES AND ENTROPIES OF DIETHYLBENZENE ISOMERS

Phase	ΔH_p (kJ/mol)	$-\Delta H_p + \Delta H_m$ (kJ/mol)	$\Delta S_p - \Delta S_m$ (J ^o K·mol)	$-\Delta H_p + \Delta H_0$ (kJ/mol)	$\Delta S_p - \Delta S_0$ (J ^o K·mol)
I	-41.6	0.52	-0.30	0.02	-0.39
II	-32.5	2.19	-3.82	2.19	-4.94
III	-33.6	2.26	-3.83	1.53	-3.27
V	-36.6	1.83	-2.13	1.83	-3.13
VI	-33.5	2.64	-4.23	3.11	-6.30
VII	-36.9	1.42	-1.46	1.02	-1.54

TABLE V

CHARACTERISTICS OF THE CHROMATOGRAPHIC COLUMNS

Column	Phase	Chromosorb	Amount of phase on the support (%)	Column length (m)
1	IV	W AW DMCS	2	1
2	III	W NAW	2	1
3	VII	W NAW	2	1
4	II	W NAW	2	1
5	II	W AW DMCS	15	2.1
6	V	W NAW	2	1

highest for the isotropic phase. In the separations of *para*- and *meta*- and *para*- and *ortho*-isomers the enthalpy factor plays a major rôle, that rôle being greater in the former than in the latter one (except for phase VI). In the separation of *ortho*- and *meta*-isomers the entropy factor is most important.

THE SEPARATING PROPERTIES

The separating properties of liquid-crystalline stationary phases possessing naphthalene groups were investigated in the systems listed in Table V. The separations were carried out using argon as the carrier gas and flow-rates of 25 cm³/min. The injector temperature was 300°C and that of the detector was 220°C. The columns were glass tubes of 4 mm I.D. The stationary phases were deposited on the support from a chloroform solution. The columns were conditioned for 3 h at a temperature 20–30°C lower than the mesophase–isotropic liquid transition temperature.

All the present naphthalene-containing phases have a common fragment in their molecules but differ as regards the terminal groups. If one substituent is constant, e.g., CH₃O–, and the second one varies, e.g., –NO₂, –OC₆H₁₃, –C₄H₉, as in columns 1, 2 and 4, then the mesophase range varies in accordance with prediction. The nitro group increases the temperature at which the mesophase occurs and decreases its range. The alkoxy group gives the widest mesophase range and intermediate values of the absolute melting and clearing temperatures. The alkyl group gives the lowest melting and clearing temperatures, the mesophase range being inter-

mediate between that of the compound with the nitro group and that with the alkoxy group. Columns 3 and 6 contain the stationary phases with the widest mesophase ranges.

Attempts to separate the isomers of methylnaphthalene, dimethylnaphthalene, bromonaphthalene, ethylnaphthalene, naphthylamine, naphthol as well as of polycyclic aromatic hydrocarbons were carried out on all columns. It was thought that the presence of the naphthalene fragment in the liquid-crystalline stationary phases would be particularly useful for separating isomers of naphthalene derivatives.

We failed to separate 1- and 2-methylnaphthalene, 1- and 2-bromonaphthalene or 1- and 2-ethylnaphthalene on any of columns 1–4 or 6, which were 1 m long and contained 2% of the stationary phase on the support. The separation of dimethylnaphthalenes depended on the composition of the mixture to be separated. However, good separations of naphthylamines and naphthol were achieved. Various temperatures were employed, beginning from the solid-to-mesophase transition point and over a wide range of the mesophase, as well as in the super-cooled state. Among the polycyclic aromatic hydrocarbons, those with smaller molecules showed better separations. The separation deteriorated or even failed altogether with increasing molecular weight, which is accompanied by significant increases in retention times.

The results obtained for the individual stationary phases are now discussed.

Column 1

The maximum temperature of the column at which the bleeding of stationary phase was reasonable was 230°C. In view of the high melting point of the liquid crystal it seemed that it would be particularly suitable for separating polycyclic aromatic hydrocarbons. The results obtained did not support this expectation, however. In the mesophase temperature range the pair phenanthrene–anthracene could not be separated. Poor separation of fluoranthene and terphenyl was possible only at the phase transition temperature; a change of temperature of several degrees resulted in no separation. The retention times are short for two- and three-ring hydrocarbons and disproportionately longer for hydrocarbons with larger numbers of rings.

In the supercooled state, separation of dimethylnaphthalene isomers was not achieved since they were all eluted in the form of one wide peak with weakly developed inflections. Methylnaphthalenes, bromonaphthalenes and ethylnaphthalenes also could not be separated. Good separation was obtained of naphthylamines (lowering of the temperature improved the separation) and of naphthols; for the latter, symmetric peaks were obtained at short analysis times. In the supercooled state, good separation was also obtained of naphthalene, diphenyl, acenaphthene and fluorene.

Column 2

As with column 1, no separation was obtained of methyl-, ethyl- or bromonaphthalenes. The separation of dimethylnaphthalenes was better, although still unsatisfactory. A mixture of eight dimethylnaphthalenes yielded three peaks; a mixture of four isomers gave three distinct peaks and one weakly developed peak. At the phase transition temperature, complete separation of naphthylamines was obtained, but the analysis time was fairly long (about 36 min). The analysis time could be shortened by raising the column temperature, when the separation is only slightly inferior. In the temperature range 160–180°C separation of 1- and 2-naphthols is

obtained in a fairly short time but the peaks are less symmetric (they have tails) than those obtained on column 1. On column 2 partial separation was obtained of the phenanthrene-anthracene pair and good separation of the mixture of naphthalene, diphenyl, acenaphthene and fluorene. In view of the fairly low upper temperature (180°C) of column operation, the retention times of successive hydrocarbons, such as fluoranthene, terphenyl, pyrene, etc., increase considerably but these compounds are well separated.

Column 3

This column, in view of the wide mesophase range and high clearing point of the stationary phase, should be useful for separating polycyclic aromatic hydrocarbons. In practice, however, the upper temperature range (in which the column can be used is 180–200°C, since above 200°C the carrier gas removed considerable amounts of the stationary phase. If that temperature is maintained for a prolonged time, decomposition of the stationary phase probably takes place, as can be seen after removal of the column from the apparatus, the packing having changed colour. The separations obtained on this column were very much the same as those on column 2. For instance, the separation of naphthylamines is good, the peaks of naphthols are asymmetric (this being greater than in the case of column 2 and methyl-, ethyl- or bromonaphthalenes could not be separated. The separation of dimethylnaphthalenes is the same as on column 2. Partial separation of the phenanthrene-anthracene pair is obtained only at the phase transition point and with long retention time. The separations of the remaining polycyclic aromatic hydrocarbons are similar to those achieved on column 2.

Column 4

Good separation of dimethylnaphthalenes was obtained (four peaks for a four-component mixture). At 160°C complete separation of naphthylamines was achieved in about 16 min. Also, naphthols were well separated, although the peaks are asymmetric. Phenanthrene and anthracene are well separated but their retention times, in view of the fairly low maximum temperature (160°C) to which the stationary phase may be heated, are fairly long. This temperature limitation does not allow separation of polycyclic aromatic hydrocarbons. The separation of the mixture of naphthalene, diphenyl, acenaphthene and fluorene is good.

Column 5

In view of the fairly poor separation and short retention times for methyl-naphthalene derivatives obtained on the columns described above, we decided to attempt the separation of naphthalene derivatives on a longer column (2.1 m) with a larger amount (15%) of the stationary phase on the support. For this purpose we used phase II, which had already been used in column 4 and seemed to give good results. Our expectations were confirmed. 1- and 2-methylnaphthalenes were separated, the latter being eluted first. Complete separation was obtained of 1,3-, 1,4-, 1,2- and 1,8-dimethylnaphthalenes, of 1,2- and 1,5-dimethylnaphthalenes and partial separation of 1,6- and 2,6-dimethylnaphthalenes. The 2,6- and 1,3- as well as the 1,5- and 2,3-dimethylnaphthalene isomers could not be separated. In view of the long retention times, no attempts were made to separate other isomers on this column.

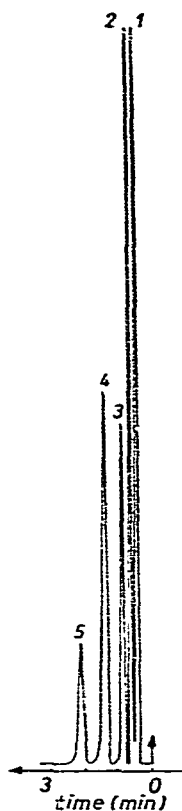


Fig. 3. Separation of polycyclic aromatic hydrocarbons on column 1 at 180°C. Peaks: 1 = benzene; 2 = naphthalene; 3 = diphenyl; 4 = acenaphthene; 5 = fluorene.

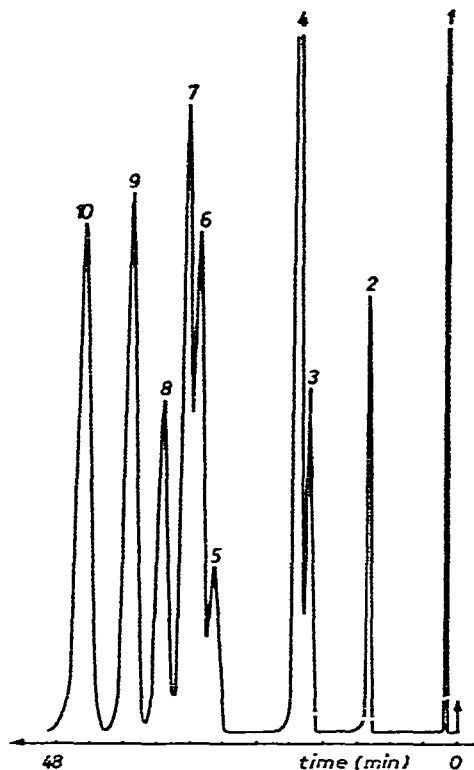


Fig. 4. Separation of polycyclic aromatic hydrocarbons on column 6 at 200°C. Peaks: 1 = benzene; 2 = phenanthrene; 3 = anthracene; 4 = fluoranthene; 5 = terphenyl; 6 = pyrene; 7 = triphenylene; 8 = 1,2-benzanthracene; 9 = chrysene; 10 = naphthacene.

Column 6

This column contained liquid crystal V having a high phase transition temperature. It was found that this phase may not be used at temperatures exceeding 220°C. The optimal temperature to which this column may be heated is 200°C, however, at this temperature the retention times for polycyclic aromatic hydrocarbons (especially of a mixture of hydrocarbons higher than phenanthrene) are very long. The separations are good, however. The separations of methylnaphthalene derivatives are similar to those obtained on columns 2 and 3. Ethyl- and bromonaphthalenes were not separated, but naphthylamines were well separated. The naphthol peaks are asymmetrical. The mixture of phenanthrene, anthracene and carbazole was well separated.

In Figs. 3–5 examples of separations of mixtures on naphthalene liquid-crystalline stationary phases are presented.

The results of the investigations described show that at least some of the phases tested may find practical application. Preliminary investigations have shown that improved separating properties can be achieved by mixing the stationary phases.

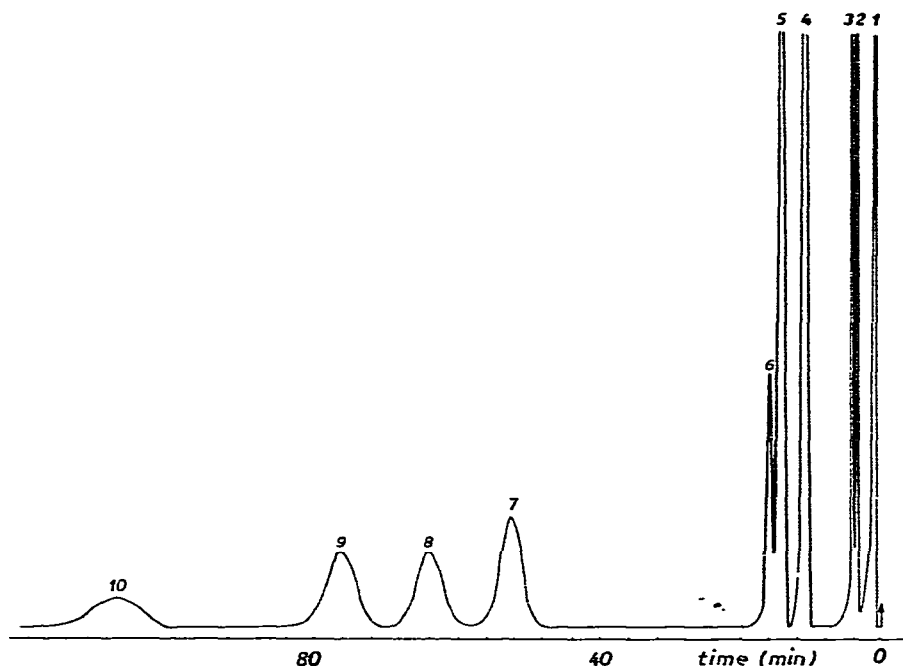


Fig. 5. Separation of methylnaphthalene derivatives on column 5 at 167°C. Peaks 1 = benzene; 2 = naphthalene; 3 = 2-methylnaphthalene; 4 = 1-methylnaphthalene; 5 = unknown; 6 = 1,3-dimethylnaphthalene; 7 = 1,6-dimethylnaphthalene; 8 = 1,5-dimethylnaphthalene; 9 = 1,2-dimethylnaphthalene; 10 = 1,8-dimethylnaphthalene.

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