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SELECTIVITY AND CHEMICAL STRUCTURE OF NEMATIC MESOPHASES IN GAS CHROMATOGRAPHY

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SUMMARY

The retention behaviour of geometrical isomers and Rohrschneider compounds was measured in the nematic range of liquid crystalline stationary phases having different chemical structures, in order to determine the influence of these structures on the polarity and selectivity of the phases. It was found that lateral substituents in mesogenic molecules effect a change in selectivity. The polarities of these phases are compared with those of conventional stationary phases, and the strong influence of the terminal groups of the liquid crystal molecules on **AI** values is discussed.

INTRODUCTION

Analytical separations have been performed successfully with liquid crystalline stationary phases. Their selectivity is affected both by the structure of the mesophase, which interacts with the substrates, and by the chemical structure of the liquid crystal. It is well known that conventional stationary phases in gas chromatography (GC) exhibit different interactions with substrates of different polarities.

The influence of different terminal substituents of liquid crystalline compounds on selectivity has been investigated. Depending on their sizes, lateral substituents in mesogenic molecules can also effect changes in selectivity^{1,2}. Using four liquid crystalline compounds of different chemical structures, we have now investigated the influence of molecular structure on polarity and selectivity in gas chromatography.

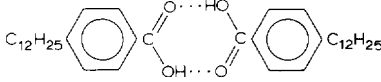
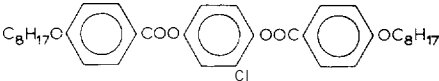

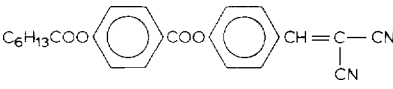
EXPERIMENTAL

Measurements were carried out with a GCHF 18.3. gas chromatograph equipped with a flame ionization detector (VEB Chromatron, Berlin, G.D.R.) using glass columns (3 m × 3 mm I.D.) packed with Chromosorb W HP (So-100 mesh), coated with about 5% of one of the liquid crystalline stationary phases listed in Table I. As substrates, geometrical isomers as well as Rohrschneider compounds were chosen.

TABLE I

STRUCTURES AND TRANSITION TEMPERATURES OF STATIONARY PHASES STUDIED

K = crystalline, Sc = smectic C, N = nematic, I = isotropic.

Phase	Name	Structure	Transition temperatures (°C)
I	4- <i>n</i> -Dodecylbenzoic acid		K 95 Sc 99 N 107.5 I
II	2-Chlorohydroquinone-bis(4- <i>n</i> -octyloxy benzoate)		K 88 N 160 I
III	Hydroquinone-bis(4- <i>n</i> -hexyloxy benzoate)		K 125 N 210 I
IV	4- <i>n</i> -Hexanoyloxy-[4-(2,2-dicyanoethenyl)-phenyl ester]		K 84 N 102 I

RESULTS AND DISCUSSION

Measurements were carried out in the nematic range at 99°C. As shown in Table II, the selectivity, α , of the compounds for separating *p*-/*m*-xylenes decreases from phase III through II and IV to I. The higher a value for phase III compared to II can probably be attributed to a stronger mutual interaction of the liquid crystal molecules, which is hindered in II by the lateral chlorine substituent. Thus differences in the geometrical structures of substrate molecules become more apparent on phase III than on II, because only molecules with favourable length/diameter ratios are able to enter into the mesomorphic structure of III. This assumption is supported by results of Panse³, who observed a decrease in selectivity for *p*-/*m*-xylenes after replacing a laterally bonded chlorine atom of 2-halogeno-4,4'-disubstituted azobenzenes by bromine.

TABLE II

SELECTIVITY, α , FOR GEOMETRICAL ISOMERS IN THE MESOMORPHIC RANGE OF PHASES I-IV AND ON OV-225 AT 99°C

Isomers	I	II	III	IV	OV-225
<i>p</i> -/ <i>m</i> -Xylene	1.00	1.04	1.08	1.01	0.98
<i>p</i> -/ <i>m</i> -Chlorotoluene	1.01	1.10	1.13	1.03	1.02
<i>p</i> - <i>m</i> -Diethylbenzene	1.10	1.18	1.20	1.09	1.04
<i>trans</i> -/ <i>cis</i> -Decaline	0.75	0.78	0.78	0.73	0.70

TABLE III

AI VALUES OF ROHRSCHEIDER COMPOUNDS ON PHASES I-IV AND ON OV-225 AT 99°C
AZ values relative to squalane.

Compound	Z	zz	III	IV	0 v-225
Benzene	63	116	144	205	205
Butanone	122	158	202	322	321
Ethanol	179	190	249	331	380
Nitromethane	160	269	338	477	511
Pyridine	—	175	295	350	373

Considering the substrates tested, with the exception of chlorotoluenes and diethylbenzenes, the boiling points of the benzene derivatives are higher for *meta* than for *para* and *ortho* isomers. Under the conditions of the structure of the mesophase a change in retention sequence between *m*- and *p*-isomers of xylenes, bromotoluenes, methylanisoles and cresoles takes place, whereas chlorotoluenes are separated according to their boiling points. Generally, owing to the influence of the nematic structure, the *p*-isomers are eluted last, in accordance with their geometries. The large difference in the boiling points of the isomeric decalines does not permit an inversion of the elution sequence to *trans* after *cis*, but a selectivity of the mesophase can be established from the later elution of the *trans*-compound.

Comparing the polarities of the phases, the *AI* values decrease from phase IV to I (Table III). Accordingly the polarity is strongly affected by the terminal substituents. The much lower values of phase I result on the one hand from the large number of CH₂ groups in the terminal substituents, which give the phase a structure resembling that of aliphatic hydrocarbons and on the other hand the carboxylic groups seem to be strongly hydrogen bonded and unable to contribute to the polarity⁴. This fact could also explain the formation of clusters of polymers of these molecules⁵. The high polarity of phase IV can be explained by the influence of the polar 2,2-dicyanoethenyl group. It is comparable to that of the moderately polar stationary phase

TABLE IV

RETENTION INDICES OF GEOMETRICAL ISOMERS IN THE NEMATIC RANGE OF PHASES I-IV AND ON OV-225 AT 99°C

Isomer	Z	zz	zzz	IV	0 v-225
m-Xylene	932	985	1012	1082	1058
p-Xylene	931	994	1023	1083	1056
o-Xylene	958	1017	1046	1121	1099
m-Chlorotoluene	1033	1101	1135	1212	1190
p-Chlorotoluene	1035	1116	1153	1216	1194
o-Chlorotoluene	1026	1091	1126	1196	1178
m-Diethylbenzene	1089	1126	1150	1223	1228
p-Diethylbenzene	1102	1150	1179	1236	1235
o-Diethylbenzene	1106	1148	1174	1255	1255
<i>trans</i> -Decaline	1103	1127	1134	1142	1151
<i>cis</i> -Decaline	1143	1163	1173	1192	1210

OV-225, whereas phases III, II and I correspond to silicone phases OV-25, OV-17 and OV-7 of low polarity.

A comparison of the retention indices of the substrates investigated on phase IV and on the conventional phase OV-225 emphasizes the influence of the liquid crystal structure (Table IV).

Contrary to results of Witkiewicz *et al.*⁶, on the more selective phases III and II the retention orders followed those of the boiling points.

CONCLUSIONS

Lateral substituents in mesogenic molecules effect a change in selectivity by varying the distance between the liquid crystal molecules. The needed optimum distance between the molecules of stationary phase, which permits the infiltration of only the *p*-isomeric substrate, is different and depends on the volume of the substrate. The polarity of mesomorphic stationary phases is strongly dependent on the nature of their terminal substituents.

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