of gas chromatography with Carbowax 20M as the liquid phase. Generally, the rearrangements were completed immediately after contacting the epoxy ester **1** with the catalyst. Under some of the conditions, however, the reactions were slower; the approximate reaction times are included in the table. The combined yields of the aldehydic ester **2** and the tetrahydrofurfuryl ester **3** were greater than 90% when benzene or ethyl ether was employed as the solvent.

Rearrangement of 4,5-Epoxy-2,2-dimethylpentyl Acetate (12).—A solution of **12** (34.4 g.) in ethyl ether (100 ml.) was added dropwise over a period of 20 min. to 44 ml. of a 10.5% (wt./vol.) solution of boron fluoride etherate in ethyl ether. The temperature was controlled to maintain a gentle reflux during the addition of the epoxy ester and until the reaction was completed (10 min.). The mixture was washed with sodium acetate solution and then with water. Distillation of the mixture gave a fraction (16 g.) distilling at 72–76° (4.2 mm.) which consisted of a binary mixture of 75% of tetrahydro-4,4-dimethylfurfuryl acetate (**13**) and 25% of tetrahydro-5,5-dimethyl-3-pyranyl acetate (**14**). An unidentified viscous oil remained after the distillation of **13** and **14**. Products **13** and **14** were isolated by means of a preparative gas chromatographic column. Infrared spectra showed the presence of a carbonyl group (5.8 μ) and the absence of a hydroxy group in each of the two compounds. The boiling point range of the binary mixture and elemental analyses of the isolated components indicated that both products were isomeric with the starting epoxy ester **12**. Their identifications were completed by n.m.r. analyses. The n.m.r. spectrum for **13** showed multiplet peaks with an area equivalent to three protons $(\text{—O—}\overset{|}{\mathrm{C}}\mathrm{H}\text{—}\mathrm{CH_2}\text{—O—}\overset{|}{\mathrm{C}}\mathrm{{=}O})$ at 4.15, single peak with an area equivalent to two protons $(\text{–}\mathrm{OCH_2}\text{–})$ at 3.47, multiple peaks accounting for two protons $(\text{–}\mathrm{CH_2}\text{–})$ centered at 1.60, single peak for the three protons of the acetyl group at 2.01, and single peak for six protons $(>\mathrm{C}<\begin{smallmatrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{smallmatrix})$ at 1.12 p.p.m. (*Anal.* Calcd. for $C_9H_{16}O_3$: C, 62.8; H, 9.4. Found: C, 62.4; H, 9.3.) The n.m.r. spectrum of **14** showed multiple peaks $(\text{—}\overset{|}{\mathrm{C}}\mathrm{H}\text{—}\mathrm{O}\overset{|}{\mathrm{C}}\mathrm{{=}O})$ at 4.90 (the peak for this proton would be expected to be downfield from the $\text{–O–}\underset{|}{\overset{|}{\mathrm{C}}}\text{–H}$ proton in **13**), multiple peaks $(\text{–}\mathrm{CH_2}\text{–O–}\mathrm{CH_2}\text{–})$ at 3.0 to 4.0, singlet $(\mathrm{CH_3}\overset{|}{\mathrm{C}}\mathrm{{=}O})$ at 1.97, multiple peaks $(\text{–}\mathrm{CH_2}\text{–})$ centered at 1.50, and two singlets $(>\mathrm{C}<\begin{smallmatrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{smallmatrix})$ at 1.04 and 0.95. The areas for the various peaks of this spectrum were also consistent with the number of protons involved in the above assignments. (*Anal.* Calcd. for $C_9H_{16}O_3$: C, 62.8; H, 9.4. Found: C, 62.8; H, 9.3.)

Hydrogenolysis of Tetrahydro-2,4,4-trimethylfurfuryl Alcohol (5).—A mixture of 19 g. of tetrahydro-2,4,4-trimethylfurfuryl alcohol (**5**), 225 ml. of cyclohexane, and 5 g. of copper chromite (Harshaw Cu-1106P) was heated in a stirred autoclave for 18 hr. at 250° and 5000-p.s.i. hydrogen pressure. After the catalyst was filtered, the product was distilled to give 8.5 g. of 2,2,4-trimethyl-1,5-pentanediol (**7**), b.p. 93–97° (1.2 mm.), $n^{20}\mathrm{D}$ 1.4565. Gas chromatographic analysis of the lower boiling fractions (9.8 g.) indicated the presence of unreacted tetrahydro-2,4,4-trimethylfurfuryl alcohol (5.1 g.), tetrahydro-2,2,4,4-tetramethylfuran (2.1 g.), and an unknown component (1.2 g.) tentatively identified as tetrahydro-3,3,5-trimethylpyran from its n.m.r. spectrum.

Analysis for Oxirane Oxygen.—The epoxy compounds were analyzed for oxirane oxygen by a modification of the King[8] procedure as described by Jungnickel, *et al.*[9] Phenolphthalein was used as the indicator for the titration of the hydrogen chloride solution.

Gas Chromatographic Columns.—Columns 6 ft. in length were constructed from 0.25-in. aluminum tubing coiled in a cylindrical spiral. The columns were packed with 40–50-mesh Chromosorb W containing 10% either of Carbowax 20M or of silicone GE-SF 96-40 as the liquid phase. Hydrogen was employed as the carrier gas at a flow rate of 90 cc./min. The detector was a thermal conductivity cell, the output of which was measured by a recording potentiometer.

N.m.r. Spectra.—The n.m.r. spectra were recorded by using a Varian Associates A-60 (60 Mc./sec.) spectrometer. The chemical shift positions were determined relative to tetramethylsilane as an internal standard.[10]

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[8] G. King, *Nature*, **164**, 706 (1949).

[9] J. L. Jungnickel, E. D. Peters, A. Polgar, and F. T. Weiss, "Organic Analysis," Vol. I, J. Mitchell, Jr., I. M. Kolthoff, E. J. Proskauer, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1953, p. 135.

[10] The n.m.r. spectra were recorded and interpreted by Dr. V. W. Goodlett.

Liquid Crystals as Solvents. II. Further Studies of Liquid Crystals as Stationary Phases in Gas–Liquid Chromatography[1]

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Six nematic and/or smectic compounds have been evaluated as liquid phases for the separation of benzene position isomers by gas–liquid chromatography. All of these gave better separations of *meta* and *para* isomers than a conventional silicone liquid phase, and the *para* isomer was invariably eluted last. Two of the compounds, 4,4′-bis(4-methoxybenzylideneamino)-3,3′-dichlorobiphenyl and *p*-phenylene bis-4-*n*-heptyloxybenzoate, were particularly effective. Two cholesteric compounds were also examined.

Liquid crystals[2] are unusual states of matter, intermediate between crystalline solids and normal isotropic liquids. Mechanically they behave as liquids, but the molecules in them possess some order in that they cannot rotate freely. The molecules of a typical liquid crystal are rod-shaped and are constrained to lie parallel, rotation being permitted only about the long axis; materials of this kind behave therefore as anisotropic liquids and are normally birefringent. Two main types of liquid crystals are known; nematic liquid crystals, in which the only restraint on the molecules is the restriction of their rotation indicated above, and smectic liquid crystals, in which the molecules are further constrained to move in layers. Smectic liquid crystals indeed have a layer structure, somewhat analogous to that of graphite.

Liquid crystals should show unusual solvent properties, due to the ordered arrangement of their molecules. One obvious consequence of this is that foreign substances should dissolve more easily in liquid crystals, the more easily their molecules fit into the liquid crystal "lattice"; different position isomers in particular should show different solubilities in liquid crystals, owing to the differences in shape between their molecules.

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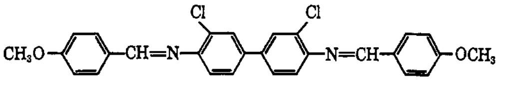
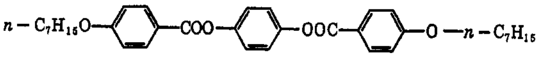
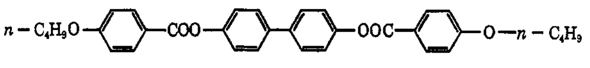
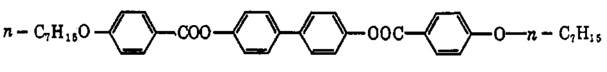
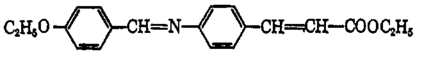
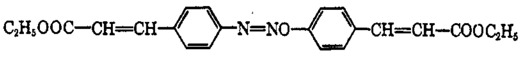
[1] This research was supported by grants from the National Science Foundation and The Robert A. Welch Foundation.

[2] G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press Inc., New York, N. Y., 1962.

TABLE I

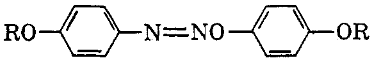
MESOMORPHIC STATIONARY LIQUID PHASES

Compd.	Structure	Smectic range, °C.	Nematic range, °C.	Cholesteric range, °C.
II		...	154–334 dec.	...
III		83–125	125–206	...
IV		171–184	184–358 dec.[a]	...
V		150–211	211–316	...
VI		78–118, 118–157[b]	157–160	...
VII		140–251 dec.	...	...
VIII	Cholesteryl benzoate	...	...	149–180
IX	Cholesteryl nonanoate	(75)[c]	...	79–90

[a] Nematic phase decomposes before transition to isotropic liquid. [b] This compound has two distinct smectic phases. [c] Monotropic (cholesteric → smectic) transition which is observed at 75° only on cooling.

The linear isomers should dissolve more easily, their molecules resembling more closely the rod-shaped molecules of the solvent.

Their reasoning led us to try[3] liquid crystals as stationary phases in gas chromatography for separating benzene position isomers. At about the same time, Kelker[4] initiated a similar investigation. Our preliminary studies using 4,4′-dialkoxyazoxybenzenes (I) as liquid phases were most encouraging, and we were able in this way to resolve several mixtures of isomers that are very difficult to separate on conventional columns. The potentialities of this technique were, however, limited by the relatively short liquid crystalline temperature ranges (<60°) and low transition temperatures to normal liquids (127–135°) shown by I. Materials with low transition temperatures are also unsatisfactory for another reason; a low transition temperature implies that the forces maintaining the ordered arrangement of molecules in a liquid crystal are relatively weak, and in such a case the discrimination between solvents on the basis of molecular shape should be relatively poor. In support of these arguments, Kelker[4] found that *p*-azoxyphenetole was more selective as a liquid phase than Ia and much more selective than diethyl azoxybenzoate. The liquid crystalline ranges of these compounds are 138–168°, 121–135°, and 114–120°, respectively. It appears that the materials of choice should be compounds with long liquid crystalline ranges and with high transition temperatures to normal liquids.



Ia, R = CH_3
b, R = n-C_6H_{13}
c, R = n-C_7H_{15}

This paper describes a study of six compounds which met these criteria, and which are listed, together with their melting points and transition temperatures, in Table I. The anils and the azoxy compound were known previously[2]; unfortunately, their utility is limited by relatively low thermal stability. The esters are members of a new series of liquid crystalline materials which we described recently[5]; they combine good chemical stability with long liquid crystalline ranges and high transition temperatures. Two cholesteric[2] liquid crystalline phases were also briefly examined.

Experimental Section

Materials.—The mesomorphic liquid phases were prepared as follows. 3,3′-Dichlorobenzidine, m.p. 134–135° (lit.[6] 133°), was obtained from the dihydrochloride (technical grade) by treatment with aqueous NaOH solution and extraction with benzene. Reaction of the benzidine with a small excess of anisaldehyde in refluxing absolute ethanol with acetic acid as catalyst,[7] or in refluxing benzene with slow distillation of the benzene–water azeotrope, gave 4,4′-bis(*p*-methoxybenzylideneamino)-3,3′-dichlorobiphenyl (II) which crystallized from benzene in yellow needles, m.p. 153–154°, (nematic → liquid) transition temperature 334° dec. (lit.[8] 149°, >340°).

Anal. Calcd. for $C_{28}H_{22}Cl_2N_2O_2$: C, 68.7; H, 4.5; Cl, 14.5; N, 5.7. Found: C, 68.7; H, 4.5; Cl, 14.8; N, 5.6.

The preparation of the arylene *p*-alkoxybenzoates (III–V) has been described elsewhere.[5] Ethyl *p*-nitrocinnamate was reduced to ethyl *p*-aminocinnamate with tin and hydrochloric acid in aqueous ethanol.[9] *p*-Ethoxybenzaldehyde was prepared from *p*-hydroxybenzaldehyde, ethyl iodide, and anhydrous K_2CO_3 in refluxing cyclohexanone.[10] Refluxing a solution of the amino ester, a slight excess of the aldehyde, and a catalytic amount of acetic acid in absolute ethanol[7] gave ethyl 4-(*p*-ethoxybenzylideneamino)cinnamate (VI). After two recrystallizations from ethanol, the yellow product had m.p. 78°; transitions temperatures (smectic → smectic) 118°, (smectic →

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[3] M. J. S. Dewar and J. P. Schroeder, *J. Am. Chem. Soc.*, **86**, 5235 (1964).

[4] H. Kelker, *Ber. Bunsenges. physik. Chem.*, **67**, 698 (1963); *Z. anal. Chem.*, **198**, 254 (1963). We are grateful to Dr. Kelker for drawing our attention to these papers.

[5] M. J. S. Dewar and J. P. Schroeder, *J. Org. Chem.*, **30**, 2296 (1965).

[6] P. Cohn, *Ber.*, **33**, 3551 (1900).

[7] G. W. Gray, J. R. Hartley, A. Ibbotson, and B. Jones, *J. Chem. Soc.*, 4359 (1955).

[8] C. Wiegand, *Z. Naturforsch.*, **6b**, 240 (1951).

[9] W. von Miller and F. Kinkelin, *Ber.*, **18**, 3234 (1885).

[10] G. W. Gray and B. Jones, *J. Chem. Soc.*, 1467 (1954).

nematic) 157°, (nematic → liquid) 160° (lit.[11] 80°, 114°, 153°, 159°).

p-Nitrocinnamic acid was reduced to *p*-azoxycinnamic acid with methanolic sodium methoxide or with benzoin in alkaline ethanol.[12] The acid was converted to the diethyl ester *via* the disilver salt and ethyl iodide.[13,14] Recrystallization from acetone left a small amount of unreacted *p*-nitrocinnamic acid in the product but extraction with methylene dichloride gave the pure yellow diethyl *p*-azoxycinnamate (VII), m.p. 140°, (smectic → liquid) transition temperature 251° dec. (lit.[13] 141°, 249°).

The cholesteryl benzoate (VIII) was a commercial product, m.p. 148–149°, (cholesteric → liquid) transition temperature 180° (lit.[15] 150°, 180°).

Cholesteryl nonanoate (IX) was prepared by reaction of cholesterol and nonanoyl chloride in pyridine. The product was recrystallized from glacial acetic acid: m.p. 78.5–79°; transition temperatures (cholesteric → liquid) 90°, monotropic (cholesteric → smectic) 75° (lit.[16] 80.5°, 92°, 77.5°).

The substituted benzenes and biphenyls which were chromatographed were commercial materials and were not purified further. Gas–liquid chromatography revealed major impurities in only three: *o*-ethylphenol (*ca.* 15%), *m*-tolualdehyde (*ca.* 15%), and methyl *m*-toluate (*ca.* 10%).

Apparatus.—The chromatograms were obtained with an Aerograph Hy-Fi gas chromatograph, Model 600-C. The column packings were prepared from Chromosorb W (60–80 mesh) and solutions of the liquid crystalline compounds in methylene dichloride except for Ia and VIII which were dissolved in acetone and 60–68° petroleum ether, respectively. All of the packings were 15% liquid phase by weight. The experimental columns and a commercial silicone column, which was used for comparative purposes, are described in Table II.

TABLE II

CHROMATOGRAPHIC COLUMNS[a]

Column	Length, m.	Stationary phase	Packing, g.
1	4.9	II	2.5
2	1.5	II	0.8
3	6.2	III	3.9
4	5.6	IV	1.8
5	6.4	V	3.8
6	6.3	VI	3.7
7	6.3	VII	3.6
8	7.6	VIII	3.1
9	7.6	IX	3.4
10[b]	8.8	Ia	5.1
11[b,c]	1.5	Silicone[d]	. . .

[a] The columns were made from 3.2-mm.-o.d. tubing. Numbers 8, 9, and 10 were annealed copper, the others stainless steel (type 316). [b] These columns were described in an earlier paper.[3] [c] Wilkens Instrument and Research, Inc. [d] Silicone SE-33, 5% on Chromosorb W.

Transition temperatures were determined with a Nalge–Axelrod melting point apparatus which has a viewing microscope and provision for observing birefringence.

Procedure.—The chromatographic samples were injected as 1% solutions in carbon disulfide. Because mesomorphic transition temperatures are depressed and mesomorphic ranges are narrowed by solutes,[17] small samples were used (0.05–0.2 μl. for columns 2 and 11, and 0.2–0.5 μl. for the longer columns). The injection chamber temperature was held 40–130° above that of the column. The carrier gas was nitrogen.

Results and Discussion

Table III lists the measured retention times at various temperatures for a number of benzene position isomers in columns with the eight mesomorphic compounds as stationary liquid phases. Table IV compares the relative retention time calculated from the data in Table III. Retention times for several substituted phenols and biphenyls in columns with liquid phase II are presented in Table V.

All of the nematic and/or smectic liquid phases which are described in this paper gave better separations of *meta–para* isomer pairs than did a conventional silicone liquid phase. Clearly mesomorphic compounds are capable of separating a wide variety of aromatic position isomers and will probably be found to exhibit selectivity in other systems where isomeric molecules differ in shape. For this reason, liquid crystals should find many useful applications in gas–liquid chromatography. Some outstanding examples of isomer selectivity which were observed in this work are as follows.

The nematic compound II was even more effective than the excellent[3] liquid phase Ia in separating *meta* and *para* isomers, except for the dichlorobenzenes where the performances were nearly equivalent. The retention times of *p*-cresol relative to *m*-cresol and of 2,5-xylenol relative to 2,4-xylenol were greater for II than the values reported for conventional columns,[18] while the relative retention of 4-methylbiphenyl (3-methylbiphenyl, 1.00) on II was 1.42–1.52, compared with 1.06 on Apiezon M grease.[19]

The ester III was highly selective in the lower part of its smectic range. At 68° the relative retention of *p*-xylene (*m*-xylene, 1.00) was a remarkable 1.10 and the order of elution was *meta–ortho–para*, whereas the higher boiling *o*-xylene is normally eluted last on both conventional and mesomorphic liquid phases. At 88° *p*-chlorotoluene and *p*-methylanisole had phenomenally high relative retentions based on their *meta* isomers, 1.17 and 1.33, respectively.

Our data indicate that the ability of a mesomorphic liquid phase to separate *meta* and *para* isomers has little bearing on its ability to separate *ortho* from *meta* or *para* isomers. Apparently steric effects are predominant in the former case, whereas both steric and polar effects are involved in the latter. Of the liquid crystals which have been studied, Ia seems the most effective in separating *ortho*-disubstituted benzenes from their position isomers. For example, the separation of *o*- and *m*-tolualdehyde is reported[20] to be very difficult but we were able to resolve these isomers completely on Ia.

Although they are not benzene position isomers, 3- and 4-picoline behave similarly on mesomorphic liquid phases. They are separated more effectively by compounds II–VII than by a conventional silicone liquid phase. The relative retention values of 4-picoline (3-picoline, 1.00) are particularly impressive for II (1.32) and VII (1.26).

The effectiveness of II as a stationary phase agreed with our expectations, since II has a very long nematic range (180°) and a high transition temperature (334° dec.). It is not surprising that it should be superior to the alkoxyazoxybenzenes (I) which have much

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(11) D. Vorländer, R. Wilke, U. Haberland, K. Thinius, H. Hempel, and J. Fischer, *Ber.*, **71B**, 501 (1938).

(12) H. B. Nisbet, *J. Chem. Soc.*, 2081 (1927).

(13) D. Vorländer, *Ber.*, **39**, 803 (1906).

(14) F. Meyer and K. Dahlem, *Ann.*, **326**, 334 (1903).

(15) C. Wiegand, *Z. Naturforsch.*, **4b**, 249 (1949).

(16) G. W. Gray, *J. Chem. Soc.*, 3733 (1956).

(17) J. S. Dave and M. J. S. Dewar, *ibid.*, 4305, 4616 (1955).

(18) A. B. Littlewood, "Gas Chromatography," Academic Press Inc., New York, N. Y., 1962, p. 437.

(19) G. H. Beaven, A. T. James, and E. A. Johnson, *Nature*, **179**, 490 (1957).

(20) J. C. Hill, Monsanto Co., private communication.

TABLE III

RETENTION TIMES[a] OF BENZENE POSITION ISOMERS IN COLUMNS WITH MESOMORPHIC STATIONARY LIQUID PHASE

Compd.	1, II[b]	3, III[b]						4, IV[b]			5, V[b]			6, VI[b]		7, VII[b]			8, VIII[b]	9, IX[b]	
	158°	68°[c]	88°	107°	121°	130°	155°	175°	182°	189°	157°	180°	207°	85°	122°	145°	160°	185°	155°	70°[c]	85°
	22[d]	20[d]	20[d]	26[d]	26[d]	26[d]	21[d]	18[d]	18[d]	18[d]	30[d]	22[d]	11[d]	33[d]	19[d]	26[d]	13[d]	13[d]	20[d]	20[d]	20[d]
m-$CH_3C_6H_4CH_3$	1.61	3.04	2.68	2.81	6.80	6.49		2.18	2.10	1.91	3.07	3.67	5.02	5.80	5.82		3.41		5.35	16.15[e]	12.2[e]
p-$CH_3C_6H_4CH_3$	1.67	3.28	2.82	2.90	7.10	6.79		2.16	2.12	1.92	3.13	3.73	5.13	5.82	5.90		3.43		5.39		
o-$CH_3C_6H_4CH_3$	1.72	3.26	2.83	3.10	8.08	7.55		2.21	2.16	1.97	3.29	3.91		7.06	6.78		3.65		6.00	18.85	14.3
m-$ClC_6H_4CH_3$	2.25		3.68	5.24	12.40	11.60		2.41	2.37	2.18	4.21	4.83		12.50	10.68	3.03	4.65				
p-$ClC_6H_4CH_3$	2.47		4.22	5.55	13.55	12.59		2.51	2.47	2.26	4.30	5.00		13.00	11.38	3.13	4.79				
m-$CH_3OC_6H_4CH_3$	2.93		5.35	7.15	17.85	16.20		2.59	2.58	2.32	4.89	5.50	7.00		17.14	3.93	5.78		10.40		
p-$CH_3OC_6H_4CH_3$	3.32		7.0	7.78	19.97	17.98		2.72	2.71	2.48	5.09	5.77	7.24		18.15	4.06	5.98		10.75		
m-ClC_6H_4Cl	2.99			5.56	17.88	16.45		2.65	2.62	2.39		5.82			14.89		5.65				
p-ClC_6H_4Cl	3.35			5.81	19.34	17.78		2.79	2.80	2.59		5.98			17.18		6.13				
m-$BrC_6H_4CH_3$	3.24				21.29[f]					2.52		6.43	7.98		18.20		6.21				
p-$BrC_6H_4CH_3$	3.70				23.64[f]					2.70		6.76	8.40		19.67		6.42				
o-$BrC_6H_4CH_3$	3.15				20.44[f]					2.53		6.35			17.01		6.01				
m-BrC_6H_4Cl	4.50				31.12[f]		21.08			2.94		8.05			26.11		7.91				
p-BrC_6H_4Cl	5.26				33.70[f]		22.54			3.18		8.32			30.30		8.65				
m-$CH_3C_6H_4CHO$	5.35[g]									3.18											
p-$CH_3C_6H_4CHO$	6.72[g]									3.63											
o-$CH_3C_6H_4CHO$	5.18[g]									3.15											
m-$CH_3OC_6H_4OCH_3$	7.00						29.22			3.42		9.51	10.89		56.1	9.23	12.52	8.54			
p-$CH_3OC_6H_4OCH_3$	8.59						32.26			3.80		10.28	11.62		61.3	9.52	12.95	8.79			
m-BrC_6H_4Br	7.32			15.85			34.82			3.75		11.75			46.9	7.98	11.97	8.39			
p-BrC_6H_4Br	8.68			17.00			37.42			4.20		12.28			54.5	8.99	13.26	9.20			
m-$CH_3C_6H_4COOCH_3$	8.12									3.70		10.52				8.91	12.67	8.67			
p-$CH_3C_6H_4COOCH_3$	10.65									4.40		12.29				10.40	14.56	9.84			
m-$ClC_6H_4COCH_3$	14.51									5.19		14.99					20.88	13.05			
p-$ClC_6H_4COCH_3$	18.48									6.21		17.03					23.37	14.55			
3-Picoline	3.52						13.5			2.60		5.48	6.55		11.31		9.63				
4-Picoline	4.52						15.7			2.78		6.08	6.96		12.40		11.90				

[a] Retention times are given in minutes. [b] Column (arabic numeral) and liquid phase (Roman numeral). [c] This temperature is below the normal smectic range of the liquid phase. The runs were made after cooling from above the transition temperature. The data indicate that the liquid phase had supercooled and was still smectic. [d] N_2 flow, cc./min. [e] Retention time of *m*–*p*-xylene mixture which gave a single peak. [f] N_2 flow rate, 21 cc./min. [g] N_2 flow rate, 32 cc./min.

TABLE IV

RELATIVE RETENTION TIMES[a] FOR BENZENE POSITION ISOMERS IN COLUMNS 1–11

Compd.	1, II[b]	3, III[b]						4, IV[b]			5, V[b]			6, VI[b]		7, VII[b]			8, VIII[b]	9, IX[b]		10,[c] Ia[b]	11,[c] silicone[b]
	158°	68°[d]	88°	107°	121°	130°	155°	175°	182°	189°	157°	180°	207°	85°	122°	145°	160°	185°	155°	70°[d]	85°	124–127°	100°
p-$CH_3C_6H_4CH_3$	1.05	1.10	1.07	1.04	1.05	1.05		0.99	1.01	1.01	1.02	1.02	1.03	1.00	1.02		1.01		1.01			1.03	1.00
o-$CH_3C_6H_4CH_3$	1.09	1.09	1.07	1.12	1.20	1.18		1.02	1.04	1.04	1.08	1.08		1.23	1.18		1.10		1.14	1.18	1.18	1.20	1.14
p-$ClC_6H_4CH_3$	1.12		1.17	1.06	1.10	1.11		1.05	1.05	1.05	1.02	1.04		1.04	1.07	1.04	1.04					1.09	1.02
p-$CH_3OC_6H_4CH_3$	1.16		1.33	1.09	1.12	1.11		1.06	1.06	1.09	1.04	1.05	1.04		1.06	1.04	1.04		1.04			1.10	1.03
p-ClC_6H_4Cl	1.14			1.05	1.08	1.08		1.06	1.08	1.11		1.03			1.16		1.10					1.16	1.03
p-$BrC_6H_4CH_3$	1.16				1.11					1.09		1.06	1.06		1.08		1.04					1.10	1.01
o-$BrC_6H_4CH_3$	0.97				0.96					1.00		0.99			0.93		0.96					0.92	1.02
p-BrC_6H_4Cl	1.19				1.08		1.07			1.10		1.04			1.16		1.11					1.16	1.03
p-$CH_3C_6H_4CHO$	1.27									1.17												1.23[e]	1.13[f]
o-$CH_3C_6H_4CHO$	0.97									0.99												0.92[e]	0.95[f]
p-$CH_3OC_6H_4OCH_3$	1.24						1.11			1.13		1.09	1.07		1.09	1.03	1.04	1.03				1.17	0.99
p-BrC_6H_4Br	1.20			1.07			1.08			1.14		1.05			1.16	1.13	1.12	1.11				1.17	1.02
p-$CH_3C_6H_4COOCH_3$	1.33									1.22		1.18				1.18	1.16	1.15				1.26	1.07
p-$ClC_6H_4COCH_3$	1.28									1.22		1.14					1.12	1.12				1.28	1.06
4-Picoline[g]	1.32						1.17			1.09		1.12	1.07		1.10		1.26						1.08[h]

[a] Retention times were corrected for column dead space in calculating these values; *meta* isomer, 1.00. [b] Column (arabic numeral) and liquid phase (Roman numeral). [c] The data for these columns were reported earlier[3] except for the tolualdehyde and picoline values. [d] *Cf.* footnote *c*, Table III. [e] N_2 flow rate, 28 cc./min.; retention times of isomers (min.): *meta*, 58.7; *para*, 72.2; *ortho*, 53.8. [f] N_2 flow rate, 19 cc./min.; retention times of isomers (min.): *meta*, 4.00; *para*, 4.51; *ortho*, 3.82. [g] Relative retentions are based on 3-picoline (1.00). [h] N_2 flow rate, 19 cc./min.; retention times of isomers (min.): 3-picoline, 1.44; 4-picoline, 1.54.

TABLE V

RETENTION TIMES[a] OF PHENOLS AND BIPHENYLS

(Stationary liquid phase = II)

Compd.	Col. 1, 158° 22[b]	Col. 2, 200° 20[b]
Biphenyl	22.45	2.86
3-Methylbiphenyl	29.9	3.47
4-Methylbiphenyl	45.2	4.85
o-Cresol	5.72	
m-Cresol	7.54	
p-Cresol	7.70	
2,6-Xylenol	5.89	
o-Ethylphenol	6.60	
2,4-Xylenol	8.10	
2,5-Xylenol	8.71	
2,3-Xylenol	9.90	
3,5-Xylenol	10.32	
3,4-Xylenol	13.12	

[a] Retention times are given in minutes. [b] N_2 flow, cc./min.

shorter liquid crystalline ranges and low transition temperatures (<135°). Unfortunately II decomposed rapidly above 250°, and slowly even at temperatures just above its melting point[21] when absorbed on Chromosorb W. It was this instability that led us to search for alternative materials, and so to develop the series of esters described in the previous paper.[5]

The ester III was investigated at four temperatures in its smectic range and two in its nematic range. At 68° only the xylenes were chromatographed, with the unusual results described above. The retention times were short and the peaks broad and tailing. At 88° the xylenes performed similarly but the retention times were still shorter and the peak shapes better. The chlorotoluenes and methylanisoles gave very broad tailing peaks at this temperature, the *para/meta* relative retentions being remarkably high. At 107° (middle of the smectic range) excellent symmetrical peaks were obtained and the retention times were somewhat longer. The order of elution of the xylenes and their relative retentions returned to "normal" (*i.e.*, similar to those observed with Ia) as did the relative retentions of *p*-methylanisole and *p*-chlorotoluene. At 121° [just below the (smectic → nematic) transition temperature] a marked increase in retention time compared to that at 107° was observed. This was accompanied by a significant rise in the relative retentions of *o*-xylene and the four *para* isomers which were studied at both temperatures. A further increase in temperature to 130° (or even to 155°) had no further effect on the relative retentions.

There is therefore a remarkable difference between the patterns of retention times for absorption on smectic and nematic stationary phases.[22] The discrimination by shape appears to be much more marked in the former case. This difference is further emphasized by the remarkable universal increase in retention times over the range 107–121°; evidently solubilities are generally lower in smectic III than in nematic III, but the difference is systematically less for the *para* isomers.

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(21) Columns 1 and 2 gave high background signals under these conditions. This could have been due to volatility rather than decomposition, but this seems extremely improbable in view of the high molecular weight of II and the presence in it of polar groups.

(22) The retention times imply that III must have been nematic at 121°, presumably through depression of the transition temperature (125° for pure III) by the dissolved substrate.

Both these results can be explained in terms of the greater order in smectic liquid crystals; in these the component molecules are not only constrained to lie parallel, but also to keep in layers, the molecules in each layer lying side by side. It must be more difficult for foreign molecules to insert themselves into the liquid crystal "lattice" of the more highly ordered smectic mesophase because of the greater loss of entropy which is involved.[23] This accounts for the large general increase in solubility as the transition temperature is passed. The greater molecular order in the smectic phase will also lead to a corresponding increase in discrimination on the basis of shape; this accounts for the greater selective affinity shown by smectic stationary phases for *para*-disubstituted benzenes.

On the other hand the selectivity shown by smectic III decreases markedly between 88 and 107°, as shown by the decrease in the ratio of *para/meta* retention times, and by the increase in the retention times of *o*-xylene relative to *m*- and *p*-xylene. This could be due to a partial breakdown of the smectic structure as the (smectic → nematic) transition temperature is approached; however, another intriguing possibility is that foreign molecules may "dissolve" in smectic liquid crystals by intercalation between the layers. Such solutions would be analogous to the intercalation "compounds" of graphite, and the geometric restrictions on the molecules in the interlayers would of course be less stringent than on molecules dissolved in the layers themselves. Nothing as yet seems to be known concerning the structures of smectic solutions; there are clearly many interesting possibilities here which we are at present exploring.

The differences between IV and V on the one hand, and III on the other, could well have been due to the higher column temperatures used in the former case. We have seen that III is less effective at 107° than at 88°; a further increase of 70° in the column temperature might well lead to a further marked decrease in efficiency. As we have seen, this decrease could be explained either in terms of decreased order in the smectic phase at higher temperatures, or to solution by intercalation. The latter explanation would account better for the fact that the relative retention times on V changed little with temperature.

The two remaining compounds, VI and VII, were of interest since they both have long smectic phases originating at relatively low temperatures. Compound VI was studied at the lower ends of each of its two smectic ranges. To our surprise the isomer separations were better at 122° than at 85°; so most of the runs were made at the higher temperature. Performance compared favorably with Ia for the dihalobenzenes, *o*-xylene, and *o*-bromotoluene but was inferior for the other systems. Compound VII was studied over a 40° range in the lower part of its very long smectic phase (140–251°). No significant variation in performance with temperature was observed within these limits and separations were generally poorer than those provided by VI. Again, the best results with *meta* and *para* isomers were obtained with the dihalobenzenes. Clearly the expected superiority to nematic liquid phases did not materialize.

The solubility of materials in liquid crystals will of course also depend on factors other than shape; it is therefore neither surprising nor disappointing to find cases where liquid crystals form ineffective stationary phases. Compounds VI and VII are much more polar than the esters III–V; presumably dipole–dipole interactions here outweigh the effects of geometry. This was also indicated by the exceptional efficiency with which II and VII separated the picolines, and by the fact that the picolines gave no meaningful chromatograms on Ia, due to tailing and erratic retention times.

Two cholesteric liquid phases were also examined briefly. The cholesteric mesophase is not so well understood as the smectic and nematic phases.[2] Similarities to both of the other types of liquid crystals have been pointed out but there are also properties exhibited only by cholesteric compounds. The relative retentions of *o*-, *m*-, and *p*-xylene on cholesteryl benzoate (VIII) and cholesteryl nonanoate (IX) proved to be similar to those which are obtained with conventional liquid phases. The same was true of *m*- and and *p*-methylanisole on VIII. IX also has a smectic phase but this gave the same results for the xylenes as did its cholesteric phase.

Summary

The results reported in this paper confirm our earlier suggestion[3] that liquid crystals may be of practical value as stationary phases in gas chromatography. They also confirm our earlier conclusion[3] that smectic phases are more effective than nematic phases in this respect. The series of esters[5] reported previously seems especially attractive in this connection; one, at least, of these (*i.e.*, III) seems superior to any previously tested compound for separating benzene position isomers. Since III is easily prepared and thermally stable, it may find practical applications in analysis.

The main interest of this work lies, however, in its implications. Thus, liquid crystals should be of general utility for separating position isomers; in these preliminary investigations we have studied only benzene position isomers since they are easily obtained and since extensive data already exist for their behavior on conventional columns. Moreover, the compounds we have used are obviously not the optimum ones; it should be possible to obtain materials with low melting points and very wide smectic ranges that could be far superior to III, even for the separation of benzene isomers. Finally, this work has confirmed our previous surmises that mixed smectic liquid crystals should offer a rewarding field; various aspects of this are being studied.

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[23] Kelker[4] has reported that entropies of solution in materials such as azoxyphenetole increase by *ca.* 7 entropy units on crossing the (anisotropic → isotropic) transition; similar measurements for (smectic → nematic) transitions would be of interest.