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Note

Feasibility study of high-temperature liquid crystals in wall-coated open-tubular columns*

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We previously reported[1–7] the synthesis and gas–liquid chromatographic (GLC) application of new high-temperature liquid crystals (mesophase transitions > 150°C) for improved separations of isomers of chemical classes of practical importance. While we have demonstrated improved isomer separations of steroids[5], bile acids[6], and metabolic benzo[*a*]pyrene phenols[7], the principal thrust of our work had been focused on isomers of 3–5-ring polycyclic aromatic hydrocarbons (PAHs)[1–4].

The use of low-temperature liquid crystals (mesophase transitions < 150°C) in wall-coated open-tubular columns had been reported earlier (*e.g.*, ref. 8) for low-molecular-weight aromatics (*e.g.*, disubstituted benzenes). The present study was undertaken to test the feasibility of high-temperature liquid crystals for PAH isomer separations when used as a wall coating substrate. N,N′-Bis[*p*-*n*-butoxybenzylidene]-α,α′-bi-*p*-toludine (BBBT) liquid crystal was selected for this study due to its ready solubility (in chloroform) for preparation of coating solutions, and its desirable temperature transitions[2].

EXPERIMENTAL

BBBT was prepared as reported previously[2], and was triple recrystallized from chloroform. The liquid crystal melted into a smectic phase at 159°, and had smectic–nematic and nematic–isotropic transitions of 188° and 303°, respectively. Wide-bore (0.76 mm I.D.) open-tubular columns were prepared from stainless-steel tubing (Handy and Harmon, Norristown, PA, U.S.A.), and were cleaned (chloroform, methanol, 50% potassium hydroxide solution, distilled water, 50% nitric acid, distilled water, methanol, chloroform), dried with nitrogen, and subsequently coated by a dynamic coating procedure at room temperature. The coated columns were con-

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ditioned in the gas chromatographic oven using a 1°/min temperature program to 220°C (with initial and final temperature hold times of 2–3 h each) and a helium carrier gas flow-rate of 5–10 ml/min. The PAH solutes were obtained from standard commercial sources and analyzed at four carrier gas (helium) flow-rates (3, 5, 7 and 10 ml/min) and six column temperatures. All solvents used were glass-distilled. GLC analyses were run on a Hewlett-Packard 7610A dual-flame gas chromatograph coupled to a Hewlett-Packard 3354 laboratory data system, with carrier gas flow-rate regulated with a calibrated mass flow controller. The GLC oven temperatures were calibrated by thermocouple readout to a calibrated temperature readout device. Sample volumes in the order of 0.3 μl or less were injected directly into an unmodified conventional inlet port, and attempts were not made to optimize the columns or chromatograph towards high chromatographic efficiencies.

RESULTS AND DISCUSSION

Retention data were obtained for 3-ring (fluorene, phenanthrene, anthracene) and selected 4-ring (triphenylene, benz[*a*]anthracene, and chrysene) PAH isomer mixtures on 165-m and 75-m wide-bore (0.76 mm I.D.) wall-coated BBBT columns in the nematic temperature range of the BBBT liquid crystal above 188°C. The PAH isomers in the 4-ring test mixture were selected since these three PAHs are often difficult to resolve on GLC high-efficiency wall-coated silicone columns[9] and HPLC C_{18}-bonded reversed-phase columns[10].

The resultant retention data, expressed as capacity factors (k'), are summarized in Table I. The retention data for 3-ring isomers are averages of the k' values determined at four carrier gas flow-rates (3.0, 5.0, 7.0, and 10.0 ml/min) for each isomer. The standard deviation of these average k' values ranged from 1–3%. Linear regression analysis of log k' *vs.* $1/T$(°K) for each isomer gave correlation coefficients exceeding 0.997. The separation factors (α) for consecutively eluting isomer pairs

TABLE I
CAPACITY FACTORS (k') FOR 3- AND 4-RING PAH ISOMERS ON BBBT LIQUID CRYSTAL OPEN-TUBULAR COLUMNS

PAH Isomer	*k'*										
	Column temperature (°C)										
	195		*200*		*210*		*220*		*230*		*240*
	*Column**										
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*
Fluorene	0.59	0.47	0.53	0.43	0.41	0.31	0.34	0.25	0.27		
Phenanthrene	1.53	1.21	1.34	1.07	1.02	0.77	0.79	0.62	0.63		
Anthracene	2.00	1.57	1.74	1.38	1.29	0.98	0.99	0.77	0.78		
Triphenylene				14.8		9.6	6.4	6.2		5.4	5.2
Benz[*a*]anthracene				20.6		13.0	9.7	8.2		7.0	6.6
Chrysene				26.4		16.5	12.9	10.4		8.7	8.0

* Column A: 165 m × 0.76 mm I.D.; Column B: 75 m × 0.76 mm I.D.

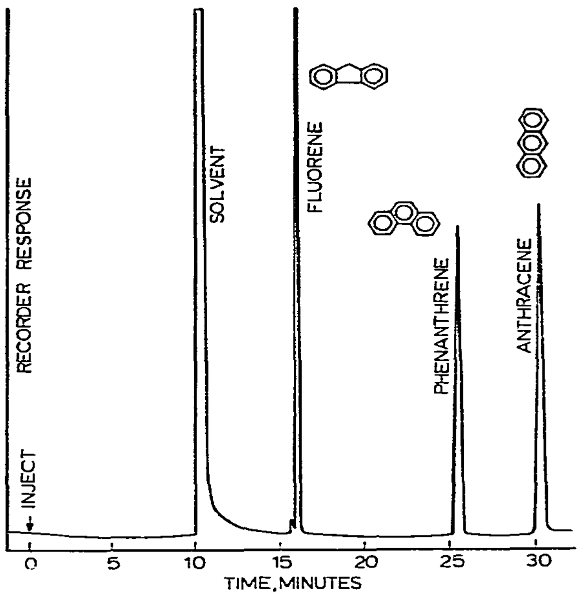

Fig. 1. Separation of 3-ring PAHs on BBBT wall-coated open-tubular column. Column: 165 m × 0.76 mm stainless steel, coated with BBBT; 195°C; carrier gas (helium) flow-rate 3 ml/min.

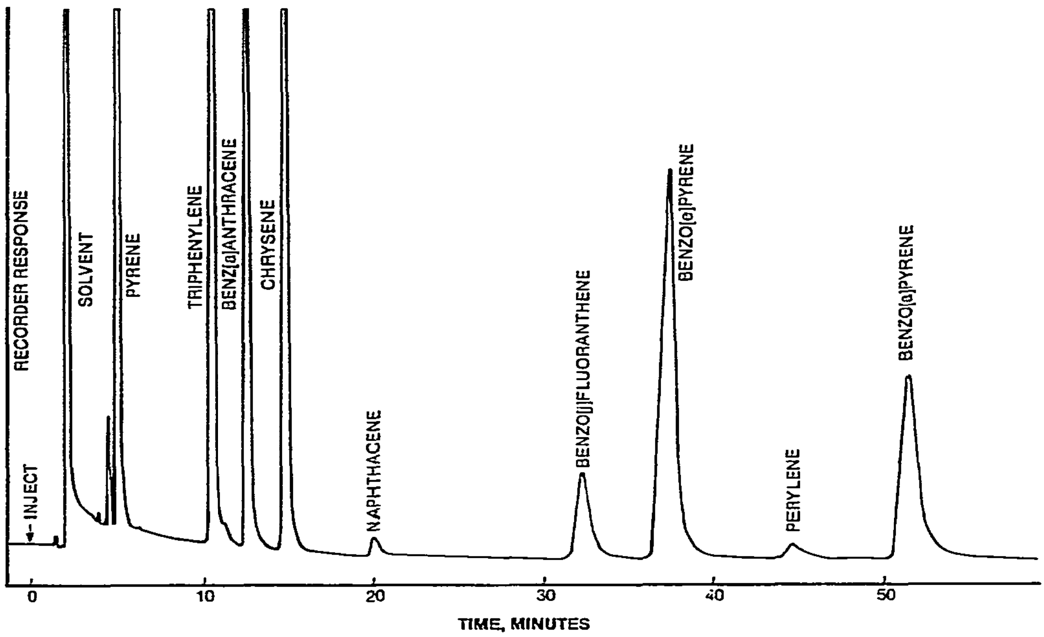

Fig. 2. Separation of 4- and 5-ring PAH isomers on BBBT wall-coated open-tubular column. Column: 75 m × 0.76 mm stainless steel, coated with BBBT; 240°C; carrier gas (helium) flow-rate 15 ml/min.

were in good agreement between the 165-m and 75-m columns, indicating little difference in relative selectivity as a function of column length. The temperature dependence of α values for isomer pairs was not large over the column temperature range studied, and useful α values were still attainable at the highest column temperatures used (*e.g.*, α[anthracene/phenanthrene] was 1.24 at 230°C; α[benz[*a*]anthracene/triphenylene] and α[chrysene/benz[*a*]anthracene] was 1.27 and 1.21, respectively, at 240°C). The separation characteristics of the wall-coated BBBT wide-bore open-tubular columns used in this study are illustrated in Fig. 1 for 3-ring PAHs (165-m column), and in Fig. 2 for a mixture of 4- and 5-ring PAH isomers (75-m column). These results are consistent with earlier findings for these isomers on packed columns[1–3], and offer evidence that a high-temperature liquid crystal used as a wall-coating substrate retains its selective capacity for the separation of PAH solute isomers.

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