High-Temperature Nematic Liquid Crystal for Gas-Liquid Chromatography

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The synthesis of three liquid crystals with the general formula N, N'-bls(p-alkoxyphenylbenzylidene)- α, α' -bi-p-toluidine where the alkoxy group is represented by methoxy (BABT; nematic range of 253–370 °C), n-butoxy (BBPT; nematic range of 232–331 °C), and benzyloxy (BBzPT; nematic range 270–346 °C) is reported. The liquid crystals were synthesized by the condensation of the appropriate 4'-alkoxybiphenyl-4-carbox-aldehyde with α, α' -bi-p-toluidine. The aldehydes were prepared by a five-step procedure starting with 4-hydroxybiphenyl. BABT was chromatographically evaluated. BABT operating in the supercooled nematic region at 230 °C provided better separations of methylbenzanthracene isomers than conventional SE-30, Dexsil 300, and Silicon Gum MS2211 columns.

The development of high-temperature liquid crystals for use as stationary phases in gas-liquid chromatography (GLC) is rapidly gaining appreciation. The topic was recently reviewed by Kelker (1) and Janini (2). Several recent applications of liquid crystal phases have been reported (3-11). Our successful use (12) of N,N'-bis(p-methoxybenzylidene)- α , α' bi-p-toluidine (BMBT; reported by Kelker (1) to be the first synthesized by Janecke and Vorlander), for the separation of three-five ring polycyclic aromatic hydrocarbons has led to its application for the separation of environmental polycyclic aromatic pollutants (13-15) and metabolites (16, 17). Steroids (18), bile acids (19), polychlorinated biphenyls (20), pharmaceuticals (21), and polynuclear azaheterocyclic air pollutants (22) were also separated by using liquid crystal phases. BMBT columns, however, have limited usefulness above 240 °C due to excessive column bleed. To overcome this problem, we undertook the synthesis of new liquid crystals (23-25). Normal chain homologues of N, N'-bis(p-alkoxybenzylidene)- α, α' -bi*p*-toluidine were prepared. Three of these liquid crystals are listed in the catalogs of the principal suppliers of chromatographic specialties. In particular, N,N'-bis(p-phenylbenzylidene)- α , α' -bi-p-toluidine (BPhBT) exhibited substantially diminished column bleed at temperatures up to 300 °C while maintaining the separation capabilities of BMBT. This improved operational stability has made BPhBT the preferred stationary phase for gas chromatography/mass spectrometry (24) and for applications in the analysis of real samples (15, 26). Moreover, the uses of BPhBT in micropacked (10) and wall-coated open-tubular columns (3) have been recently reported. It is unfortunate, however, that the utility of BPhBT to GLC applications is limited to temperatures above its solid-nematic temperature of 257 °C.

There is still a need for new liquid crystal stationary phases that combine the desired characteristics of selectivity, high resolution, thermal stability, and a wide, chromatographically useful, mesomorphic temperature range. In this paper we report some progress in our efforts to synthesize and chromatographically evaluate such phases. The new compounds are of the general formula N,N'-bis(p-alkoxyphenyl-benzylidene)- α,α' -bi-p-toluidine.

EXPERIMENTAL SECTION

Materials. The liquid crystals were synthesized as illustrated for the compound N, N'-bis(p-methoxyphenylbenzylidene)- α, α' bi-p-toluidine (BABT). To 3.49 g (0.0165 mol) of 4-methoxy-4'-biphenylaldehyde in 100 mL of absolute ethanol was added 1.73 g (0.0082 mol) of α, α' -bi-*p*-toluidine (Eastman Organics). The mixture was refluxed with stirring for 5 days. The product was collected by filtration while hot and washed with several volumes of hot ethanol and dried under vacuum, yielding 4.16 g (84%). The 4-methoxy-4'-biphenylaldehyde was prepared from 4hydroxybiphenyl (Pfaltz and Bauer Inc.) in a five-step procedure according to Gray et al. (27). 4-Hydroxybiphenyl was first converted to 4-methoxybiphenyl by treatment with dimethyl sulfate (69% yield). 4'-Acetyl-4-methoxybiphenyl was then prepared by the Friedel-Crafts acylation of 4-methoxybiphenyl (36% yield). The acetyl derivative was oxidized with sodium hypobromide to 4'-methoxy-4-biphenylcarboxylic acid (95% yield). The acid was reduced with diborane to 4-methoxybiphenyl-4-carbinol (89% yield). Finally, the carbinol was oxidized with lead tetraacetate/pyridine to 4'-methoxy-4-biphenylaldehyde (85% yield).

N,N'-bis(*p*-butoxyphenylbenzylidine)- α,α' -bi-*p*-toluidine (BB-PT) and N,N'-bis(*p*-benzyloxyphenylbenzylidene)- α,α' -bi-*p*-toluidine (BBzBT) were synthesized in a similar manner with the appropriate starting aldehyde and diamine. The respective aldehydes were prepared from 4-butoxybiphenyl and 4-benzyloxybiphenyl as described above for the methoxy homologue.

The polycyclic aromatic hydrocarbons were obtained from the International Hydrocarbon Bank, Ottawa, Canada.

Apparatus. A Hewlett-Packard 7610 gas chromatograph equipped with dual flame ionization detectors was used for this work. Helium carrier gas was regulated by a calibrated Brooks 5840 mass flow controller. Inert HP Chromosorb W was used as solid support. The packing material was prepared by the solvent slurry method (12, 24, 25). The BABT columns were conditioned at 270 °C for 2 h prior to initial use. A Perkin-Elmer Model DSC-2 was used for the determination of the liquid crystal transition temperatures. The temperature axis was calibrated with the melting points of indium (mp 156.68 °C), tin (mp 231.88 °C), and lead (mp 327.47 °C). A Mettler PF52 heating stage and FP.5 temperature control unit coupled with a Bausch and Lomb polarizing Stereozoom 7 microscope confirmed the digital scanning calorimetry (DSC) results at temperatures below 300 °C.

RESULTS AND DISCUSSION

Gray (28) demonstrated that in a nematogenic compound the substitution of a terminal hydrogen by a different functional group enhanced the thermal stability of the liquid crystalline melt; i.e., resulted in a new nematogenic compound with a higher nematic-isotropic transition temperature. On the other hand, the effect of substitution on the crystal-nematic transition temperature cannot be predicted because alterations in the molecular structure may result in unpredictable changes in the efficiency of packing in the solid state. Realizing the potential and limitations of BPhBT as a stationary phase in GLC, it was felt that its homologue BABT would lead to an improved GLC phase. Its wider nematic state would expand its chromatographically useful temperature

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Table I. Transition Temperatures (°C) for Compounds of the Type

$(R - O - CH = N - O - CH_2)_2$									
terminal substituent R	liquia crystal	molar mass	solid-nematic	nematic-isotropi	ic ΔT nematic				
H-	${f BPhBT}^a$	540	257 ± 2	403 ± 2	146				
CH ₃ O-	BABT ^b	601	253 ± 2	>370	>117				
CH ₃ (CH ₃) ₂ O-	BBPT ^c	685	232 ± 2	331 ± 2	99				
PhCH ₂ O-	BBzPt	753	270 ± 2	346 ± 2	76				
^a Reported previously, ref 24 C and smectic-solid at 218 °C.	. ^b On cooling:	nematic-smect	cic-solid at 225 °C	. ^c On cooling:	nematic-smectic at 228				

range. Moreover, the increase of about 11% in molar mass over BPhBT could reduce even further the amount of column bleed.

Table I lists the N,N'-bis(p-alkoxyphenylbenzylidene)- α ,- α' -bi-p-toluidines together with their respective liquid-crystalline transition temperatures. BPhBT was included for comparison. Since BBPT and BBzPT offer no particular advantage over BABT as is evident from the DSC results, their use in GLC was not investigated. BABT decomposes when heated to temperatures above 370 °C, and therefore, its nematic isotropic temperature could not be determined. However, a 2.5% BABT column was routinely operated in our laboratory at and below 265 °C for over a year. The same column was periodically operated at temperatures up to 290 °C without adverse effect.

It has been reported (15) that the life of BPhBT columns could be extended to months if certain experimental precautions are observed. Our experience with both column materials indicates that the BABT columns offer improved bleed characteristics over BPhBT when compared at the same temperature. The main advantage of BABT over BPhBT columns is that BABT can be operated in the supercooled nematic region down to 225 °C. Supercooling of the nematic region has been observed by several workers with packed columns containing liquid crystals (13, 29). Our DSC results indicated that when the BABT melt was cooled, a nematicsmectic transition appeared at 232 °C followed by a smectic-solid transition at 225 °C. We found that these liquid crystal transitions were independent of the cooling rate. In one DSC experiment, a BABT sample was melted and then cooled to 235 °C and then left for over 6 h. When the cooling program was continued the nematic-smectic and smectic-solid transitions appeared at the expected temperatures. In another experiment a 2.5% BABT column was heated to 270 °C and then cooled to 235 °C, at which temperature it was isothermally operated for 10 h. Repeated injections of a test solute at 235 °C under the same instrumental conditions showed no variation of solute retention time during the period of isothermal operation.

To illustrate the potential utility of BABT in its supercooled nematic region, we investigated several examples showing its application to the separation of synthetic mixtures of threefour ring polycyclic aromatic hydrocarbons and their monomethyl derivatives.

Table II gives a comparison of the relative retention behavior of methylbenz[a]anthracenes on BABT and conventional SE-30, Dexsil 300, and Silicon Gum MS 2211. The methylbenz[a]anthracenes are listed in order of decreasing retention on BABT. It was interesting to note the differences in the retention behavior between BABT and the other phases. As expected, all methylbenz[a]anthracenes were retained longer than the parent benz[a]anthracene on the nonliquid crystal columns. This is in agreement with their respective higher molar masses and consequently higher boiling points. Moreover, the selectivity of these phases toward isomeric methylbenz[a]anthracenes was poor. This was probably due Table II.Comparison of Relative Retention Data forMethylbenz[a]anthracene Solutes on BABT and ThreePolymeric Stationary Phases

	rela	ime		
compound	BABT ^a	SE- 30 ^b	Dexsil 300°	Silicon Gum (MS 2211) ^d
benz[<i>a</i>]anthracene	1.00	1.00	1.00	1.00
3-methyl-	1.97	1.35	1.39	1.44
9-methyl-	1.91	1.39	1.39	1.42
4-methyl-	1.82	1.43	1.50	1.53
12-methyl-	1.43	1.45	1.45	1.49
7-methyl-	1.37	1.52	1.66	1.66
10-methyl-	1.24	1.38	1.41	1.44
8-methyl-	1.22	1.39	1.44	1.48
5-methyl-	1.15		1.51	1.52
1-methyl-	1.08	1.29	1.37	1.37
11-methyl-	0.91	1.33	1.32	1.37
2-methyl-	0.89	1.35	1.36	1.37

 a 2.5% BABT on HP Chromosorb W (100/120) mesh supercooled at 240 °C, this work. b 5% SE-30 on HP Chromosorb W (100/120) mesh at 240 °C, this work. c 5% Dexsil 300 on HP Chromosorb W (100/120) mesh at 240 °C, this work. d 200 ft \times 0.020 in. capillary at 215 °C, ref 30.

to small differences in solute propreties which failed to affect appreciable differential solubility.

The nematic BABT phase offered enhanced selectivity toward these isomers as solute shape differences are the predominant factor in liquid crystal selectivity. As a result, the more rodlike 3-methyl- and 9-methylbenz[a]anthracenes were retained longer than the other isomers. However, the parent benz[a]anthracene with a lower molar mass was retained longer than its bulkier 2-methyl- and 11-methyl derivatives. The prevailing "rule of thumb" that the more rodlike isomer should be more soluble in nematic phases does not, however, explain the retention order of all methylbenz-[a]anthracene isomers. It was clear that because of the small differences in solute length-to-breadth ratios, the relative contribution of this steric retention mechanism was overwhelmed by other contributing factors to solubility.

For the assessment of the enthalpic contribution to selectivity toward methylbenz[a]anthracenes on BABT, corrected retention time data $(t_{r'})$ for all solutes listed in Table I were obtained at 230, 240, 250, and 260 °C on BABT, SE-30, and Dexsil 300 columns. All data on each of the phases were recorded under the same instrumental conditions so that a plot of the logarithm of t_r vs. reciprocal temperature according to the equation of Littlewood and co-workers (31) would yield a line-of-slope $(-\Delta H_s/R)$ where ΔH_s is the partial molar enthalpy of solution and R is the universal gas constant. Correlation coefficients for all plots were in excess of 0.995 and the standard deviations in the slopes were less than 1% of the respective values as determined by linear regression analysis. The resulting ΔH_s values are listed in Table III. The

Table III. Partial Molar	Enthalpies	of Soluti	on		
	$\Delta H_{\mathrm{S}},\mathrm{kJ}\mathrm{mol}^{-1}$				
compound	BABT (nematic)	SE-30	Dexsil 300		
benz[a]anthracene 3-metnyl- 9-methyl- 4-methyl- 12-methyl- 7-methyl- 10-methyl- 8-methyl- 1-methyl- 11-methyl-	-70.5 -76.2 -72.8 -68.3 -69.3 -69.2 -65.9 -68.3	-66.9 -70.1 -71.8 -71.8 -70.0 -71.2 -72.3 -70.3 -70.9 -71.2 -72.4	-67.6 -73.4 -72.1 -72.5 -72.4 -70.8 -72.1 -71.6 -72.1		



Figure 1. Separation of three-ring polycyclic aromatic hydrocarbons on BABT at 235 °C: column, 6 ft \times 2 mm i.d. glass; packing, 2.5% (w/w); flow rate, 20 mL/min; injector and detector, 250 °C.

negative sign signifies that heat is evolved when an infinite dilution transfer of solute takes place from the gaseous mixture (solute plus carrier gas) to the actual solution. Inspection of the data indicated that there was no enthalpic selectivity toward methylbenz[a]anthracenes on SE-30 and Dexsil 300. On both phases, ΔH_s values for the parent benz[a]anthracene were lower (less negative) than those of their monomethyl derivatives. In contrast, ΔH_s values obtained by using BABT ranged from 76.2 kJ mol⁻¹ for the 3- and 9-methyl- to 65.9 kJ mol⁻¹ for the 1-methyl derivative with benz[a]anthracene, assuming a value of 70.55 kJ mol⁻¹. It was clear than enthalpic differences contributed to the selectivity of BABT toward these isomeric solutes; however, there was no observed correlation between ΔH_s values and solute length-to-breadth ratios.

Further chromatographic evaluation of BABT was achieved through the separation of selected polycyclic aromatic hydrocarbons (parent compounds and monomethyl derivatives). An illustration of the separation of three-ring compounds is given in Figure 1. Figure 2 shows the separation of chrysene from two of its methyl derivatives. Separations of alkylated phenanthrenes, anthracenes, and chrysenes have not been reported previously. Some members of these classes of compounds which are found in the environment exhibit carcinogenic (30, 32-34) and mutagenic (34) properties. Therefore



Figure 2. Separation of some chrysenes on BABT at 235 °C. Column, packing, conditions same as Figure 1. Flow rate was 10 mL/min.

this application should be useful for the analysis of these compounds.

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Quantitative Separation of Samarium from Neodymium by Anion Exchange Chromatography in Dilute Nitric Acid-Methanol

Sir: The lanthanides are adsorbed by anion exchange resins from aqueous nitric acid solutions only to a small (light lanthanides) or a negligible extent (heavy lanthanides) (1-3). Differences in the values for the distribution coefficients of the light lanthanides in fairly concentrated nitric acid are much too small to allow efficient separations. The situation is improved considerably when a water-soluble nonaqueous component is added to the aqueous phase. Distribution coefficients for the light lanthanides increase very dramatically and the separation factors are also enhanced considerably. Edge seems to have been the first to use nitric acid-ethanol mixtures for the separation of elements of the lanthanide group from each other (4). Yet he did not attempt separation of adjacent members of the group in his first publication nor does the publication contain any quantitative results (4). In later work (5) describing a group separation of neodymium plus the lighter lanthanides from samarium plus the heavier lanthanides, 35% of 3.5 M nitric acid plus 65% methanol was used as the best eluting agent. Separations were quantitative for mixtures containing 200 μ g of neodymium and 50 μ g of samarium. Several percent of the neodymium appeared in the samarium fraction when 400 μ g of neodymium was present. As pointed out by Edge already (5), a better separation can be expected by using a resin of finer particle size and lower cross-linkage and, if necessary, also by using lower flow rates. Distribution data for a resin of 4% cross-linkage were published by Faris et al. (6), but their work was mainly aimed at the preparation of pure lanthanide oxide fractions and does not contain data on quantitative separations. Some other work either is mainly concerned with distribution data (7-9) or is aimed at separating trace amounts of lanthanides into groups mainly for neutron activation analysis (10-12).

In addition, some recent work which was developed for the separation of neodymium prior to its determination by isotope dilution mass spectrometry to establish the burn up rates of nuclear fuel also makes use of anion exchange in nitric acidmethanol mixtures (13-15). In some cases HPLC methods were used (16-18). All these methods were developed for the partial separation of micro- or nanogram amounts of neodymium and are not aimed at nor do they provide a quantitative separation of larger amounts of neodymium and samarium. Considerable overlapping of bands of adjacent lanthanides occurs even at very low concentrations of lanthanides (14, 15). Another more recent publication (19) presents additional information about distribution coefficients of lanthanides in nitric acid-methanol and some elution curves but makes no attempt to obtain quantitative results for a separation. Furthermore, the interesting region of low nitric acid and high

methanol concentration is not covered.

Apparently there has not been any successful attempt to separate larger amounts of neodymium and samarium and thus separate the lanthanides quantitatively into two groups by using anion exchange in nitric acid-organic solvent mixtures. Papers describing work with common microporous resins show a tendency to use relatively high concentrations of nitric acid for the separation (5-11, 12, 16). Yet the distribution data of Faris et al. (6) indicate at careful study that separation factors between adjacent lanthanides increase with increasing methanol concentration. Because distribution coefficients also increase with increasing nitric acid concentration and a high distribution coefficient for the eluted element would be impractical, the tendency to use high concentration of nitric acid seems to be surprising. In fact one should aim to make the methanol concentration as high as possible and the nitric acid concentration as low as possible while aiming at a distribution coefficient of about 10 ± 5 for the eluted element. This paper describes a method which was developed not only for the separation of trace amounts of lanthanides into two groups but for the quantitative separation of neodymium and samarium in amounts up to 100 mg and more. For this purpose it was tried to optimize experimental parameters such as resin particle size, resin cross-linkage, nitric acid and methanol concentration, and flow rate, as far as was possible and practical under the circumstances.

EXPERIMENTAL SECTION

Reagents. The resins used were the AG1-X4 and AG1-X8 strongly basic anion exchangers on polystyrene bases marketed by BIO.RAD Laboratories of Richmond, CA. Resin of 200-400 mesh particle size was used for column work. Water was distilled and then passed through an Elgastat deionizer. Neodymium, samarium, and other lanthanide oxides of $\geq 99.9\%$ purity were obtained from Fluka AG, Buchs, Switzerland. Neodymium and samarium oxide were further purified by using anion exchange chromatography in nitric acid-methanol. The final products contained less than 5 ppm of the "other" oxide respectively.

Apparatus. Borosilicate glass tubes of 21 mm bore and 42 cm length, fitted with a B19 ground-glass joint at the top and a no. 2 glass sinter plate and a tap at the bottom, were used as columns. Alternatively tubes of 12 mm bore and 30 cm length, fitted with a B12 ground-glass joint at the top were used for smaller amounts of the elements. A Carl Zeiss ultraviolet-visible spectrophotometer was used for determinations by molecular absorption spectrometry, and Varian-MAT SMIBF mass spectrograph modified as indicated previously (20) was used for mass spectrometric determinations.

Elution Curves. A column containing 58 mL (20 g dry weight) of AG1-X4 resin of 200-400 mesh particle size was converted to