Journal of Chromatography, 202 (1980) 75–82
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 13,147

GAS–LIQUID CHROMATOGRAPHIC SEPARATION OF METHOXY-SUBSTITUTED QUINONES ON NEMATIC LIQUID CRYSTALS

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(Received May 22nd, 1980)

SUMMARY

The use of liquid crystals N,N′-bis(*p*-butoxybenzylidene)-*α*,*α*′-bi-*p*-toluidine and N,N′-bis(*p*-phenylbenzylidene)-*α*,*α*′-bi-*p*-toluidine (BPhBT) as stationary phases for gas–liquid chromatographic (GLC) separations of methoxyquinones is reported. The chromatographic profiles of mono- and dimethoxyquinones having 2–5 aromatic rings are presented. The retention ratios for benzanthraquinone/1-CH_3O-/2-CH_3O-/3-CH_3O-/4-CH_3O- at 272°C on BPhBT were 1.00/1.19/1.81/3.63/2.53, and the respective resolutions were $R_{1,2} = 6$, $R_{2,3} = 5$, and $R_{3,4} = 6$. The liquid crystal columns gave better resolution with shorter elution times when compared with OV-17 columns. The orders of elution of the isomers on the liquid crystal columns were predictable from the molecular shape and substitution patterns. This should make it possible to predict molecular structure (isomer position) from the GLC retention data.

INTRODUCTION

During our development of new methods for the synthesis of polycyclic aromatic hydrocarbons (PAHs)[1–3] it has become apparent that the work would be greatly helped if the method used for analyzing the reaction products were also selective enough to give information about the structure. The order of separation obtained with nematic liquid crystal gas–liquid chromatographic (GLC) phases has been attributed to the ordered structure of the liquid crystal mesophase. These ordered structures affect the ability of solute molecules to fit or solubilize into the liquid phase, and this property is the basis of their selectivity. Molecules of nematic liquid crystals while in the nematic state align themselves in a parallel head-to-tail orientation. This orientation contributes to the separation of molecules on the basis of their length-to-breadth ratios and molecular planarity, in addition to, boiling point and polarity differences. The previous success in our laboratory using liquid crystals for the separations of PAHs[4,5] led us to investigate these phases for methoxyquinone separations.

EXPERIMENTAL

A Varian Model 1440 gas–liquid chromatograph equipped with a flame-ionization detector and a linear temperature programmer was used for this study. Chromatograms were generated on a 1-mV f.s. strip-chart recorder using an electrometer setting of 10^{-11} A/mV. The nitrogen carrier gas flow-rate was 60 ml/min, air flow-rate was maintained at 200 ml/min and hydrogen flow-rate was 30 ml/min as measured by a soap-bubbler flow-meter. Sample injection volumes were 1–2 μl. The chromatographic columns were either a 5% OV-17, 2.5% N,N′-bis(*p*-butoxybenzylidene)*α*,*α*-bi-*p*-toluidine (BBBT) or 2.5% N,N′-bis(*p*-phenylbenzylidine)*α*,*α*′-bi-*p*-toluidine (BPhBT) on 100–120 mesh Chromosorb HP, packed in 6 ft. and 3 ft. × 2 mm I.D. glass columns. The liquid crystal column packings were prepared by the solvent slurry technique and fluidized drying with nitrogen[4,5]. The liquid crystals were carefully purified and glass-distilled chloroform was used for preparing the packing by the solvent slurry technique. Oxygen and water traps were used to remove these substances from the carrier gas. Approximately 2–3 in. at the inlet/outlet ends of each column was packed with a 3–5% Dexsil 300 or SE-30 on 100–120 mesh Chromosorb W HP as terminal buffers. The addition of the conventional phase regions at the ends of each column is recommended if the columns are inserted into the injection port for on-column injection and into the detectors for reduced dead volumes.

We prepared the substituted naphthoquinones (NTQs), anthraquinones (ATQs)[6], phenanthraquinones (PhTQs)[7], benzanthraquinones (BATQs)[1–3] and dibenzanthraquinones (DBATQs)[8] as intermediates in the synthesis of substituted PAHs. Their structures were deduced from the route of synthesis, the spectral and physical data, and by chemical conversion to known compounds.

RESULTS AND DISCUSSION

We studied the separation of quinones and their methoxy isomers on the nematic liquid crystals BBBT and BPhBT and compared the results with those obtained with an OV-17 column (Table I).

The order of elution of the isomers on the liquid crystal columns always followed the same pattern. The isomers having the larger length-to-breadth ratios were retained longer. For example, the elution order BATQ < 1-CH_3O- < 2-CH_3O- < 4-CH_3O- < 3-CH_3O-BATQ was consistent with increasing length-to-breadth ratios. The elution order of BATQ < 11-CH_3O- < 8-CH_3O- = 10 CH_3O- <9-CH_3O-BATQ was also consistent. The OV-17 column gave an elution order of BATQ < 9-CH_3O- = 10-CH_3O- = 11-CH_3- < 8-CH_3O-BATQ. The elution order for the disubstituted CH_3O-BATQs using a BPhBT phase was 3,11- < 3,8- = 3,10- < 3,9-di-CH_3O-BATQs. The elution order for the disubstituted ATQs was 2,7-diCH_3O-ATQ < 2,6-diCH_3O-ATQ using a BBBT column; no separation was obtained with the OV-17 column. The magnitude of the separations, and the order of elution, was as expected from the differences in molecular shape and the length-to-breadth ratios. The order of elution for the isomers of a particular quinone (*e.g.* 1-, 2-, 3-, and 4-CH_3O-BATQ) and for unsubstituted quinones (*e.g.* ATQ, BATQ, DB[*a*,*j*]ATQ and DB[*a*,*h*]ATQ) were predictable from length-to-breath considerations. The larger the

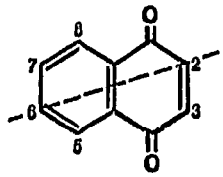
TABLE I

GLC RETENTION DATA FOR METHOXYQUINONES USING BBBT, BPhBT AND OV-17 LIQUID PHASES

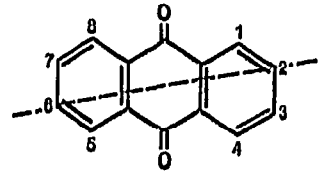
NTQ = Naphthoquinone, ATQ = anthraquinone, PhTQ = phenanthraquinone, BATQ = benzanthraquinone, DB[*a,h*]ATQ = dibenz[*a,h*]anthraquinone, DB[*a,j*]ATQ =dibenz[*a,j*]anthraquinone.

Compound	*Retention Times (min)*				
	BBBT	*BBBT*	*BPhBT*	*BPhBT*	*OV-17*
1,4-NTQ	1.27*	0.97***	—	—	—
6-CH_3O-NTQ	3.82				
5-CH_3O-NTQ	4.65				
1,4-PhTQ	4.13**	10.75	—	—	8.21**
5-CH_3O-PhTQ	4.13				17.91
6-CH_3O-PhTQ	9.64				17.91
7-CH_3O-PhTQ	14.62				22.49
8-CH_3O-PhTQ	10.70				21.40
9,10-ATQ	3.80**	9.93	—	—	4.75§§§
2-CH_3O-ATQ	12.03				11.93
2,7-diCH_3O-ATQ	36.66				31.32
2,6-diCH_3O-ATQ	45.45				31.32
BATQ	—	44.48	3.59§,+	3.48§,+	10.98§§
1-CH_3O-BATQ			4.27	4.16	18.61
2-CH_3O-BATQ			6.48	6.37	20.52
3-CH_3O-BATQ			13.02	12.91	24.95
4-CH_3O-BATQ			9.07	8.96	23.73
8-CH_3O-BATQ				8.59	26.11
9-CH_3O-BATQ				11.82	24.34
10-CH_3O-BATQ				8.59	24.34
11-CH_3O-BATQ				6.21	24.34
3,11-diCH_3O-			17.95+		
3,8-diCH_3O-			26.90		
3,10-diCH_3O-			30.60		
3,9-diCH_3O-			50.52		
DB[*a,h*]ATQ	—	—	32.67§	—	58.0§
1-CH_3O-ATQ			32.67		—
2-CH_3O-ATQ			62.04		110.0
3-CH_3O-ATQ			131.04		138.5
4-CH_3O-ATQ			75.54		131.0
DB[*a,j*]ATQ	—	—	19.56§	—	58.0§
1-CH_3O-ATQ			—		—
2-CH_3O-ATQ			35.85		110.0
3-CH_3O-ATQ			77.06		138.5
4-CH_3O-ATQ			47.35		131.0

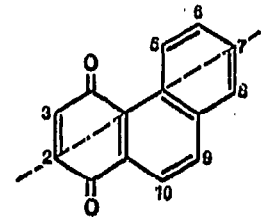
* Column temperature, 190°C.
** Column temperature, 225°C.
*** Column temperature programmed from 192 to 242°C at 4°C /min with a 15-min initial delay.
§ Column temperature, 262°C.
§§ Column temperature, 210°C.
§§§ Column temperature, 226°C.
\+ Separate mixtures of isomers



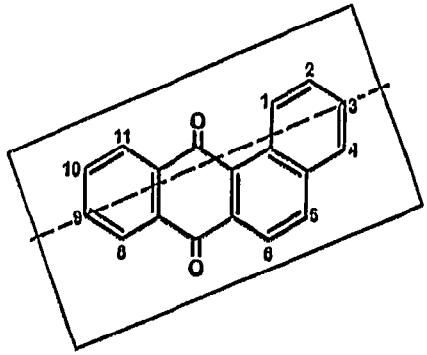
1,4-NTQ



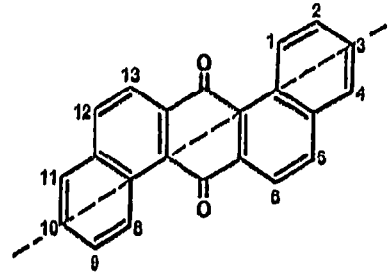
9,10-ATQ



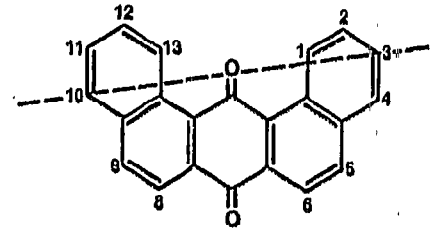
1,4-PhTQ



7,12-BATQ



7,14-DB[a,h]ATQ



7,14-DB[a,j]ATQ

Fig. 1. Structures and numbering used for the methoxyquinones studied.

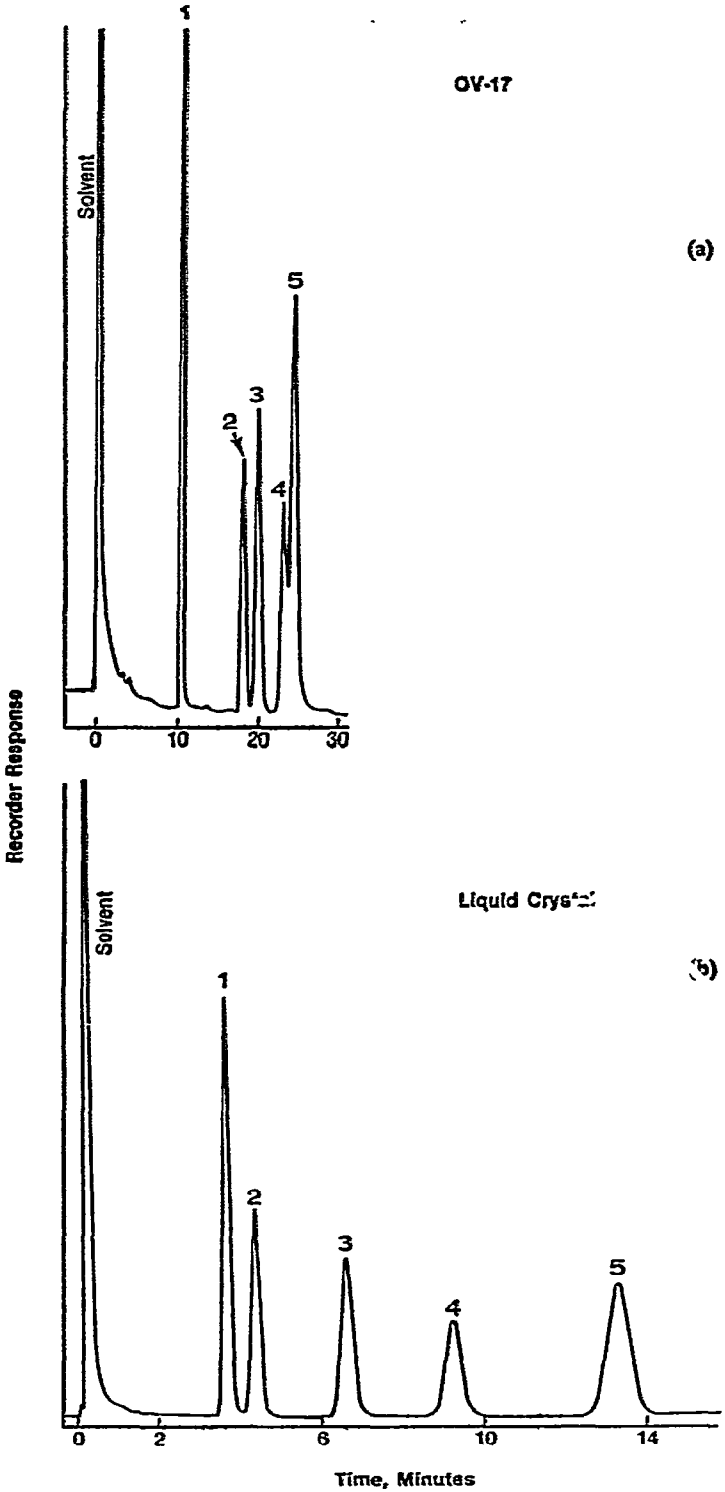


Fig. 2. Chromatograms of 1-, 2-, 3- and 4-methoxybenzanthraquinones. (a) Column: 6 ft. × 2 mm I.D.; packing: 5% OV-17. Conditions: oven 262°C; flow-rate 60 ml/min. (b) Column: 6 ft. × 2 mm I.D.; packing: 2.5% BPhBT. Conditions: oven 262°C; flow-rate 60 ml/min. Peaks: 1 = 7,12-BATQ; 2 = 1-CH_3O-BATQ; 3 = 2-CH_3O-BATQ; 3 = 4-CH_3O-BATQ; 5 = 3-CH_3O-BATQ.

contribution from the methoxy substituent to increasing the length instead of the breadth of this imaginary rectangle (Fig. 1 and Table I, 7,12-BATQ example) the longer the retention time. When the methoxy substituent contributed to the breadth of the molecule, the retention times were shorter. The line drawn between the 3- and 9-positions of BATQ connects the position with the longest retention times (Table I) and should divide this imaginary rectangle. The same exercise can be done with all the methoxyquinones in Table I. This method of predicting elution order holds for the unsubstituted quinones as well as those that are substituted. If 9,10-ATQ is considered to be the parent compound (Fig. 1) then extending its length with the addition of aromatic rings should increase the retention time in a predictable manner. The observed order of elution is ATQ < BATQ < DB[*a,j*]ATQ < DB[*a,h*]ATQ as expected. This type of consistent elution is potentially useful in predicting structural information of closely related isomeric compounds.

The retention ratios and resolutions of the mono- and dimethoxy isomers were considerably better using the liquid crystal columns than with OV-17. This is illustrated by the separation of the 1-, 2-, 3-, and 4-CH_3O-BATQ in Fig. 2. The retention ratios for these isomers using BPhBT were 1.00/1.52/3.05/2.12 compared

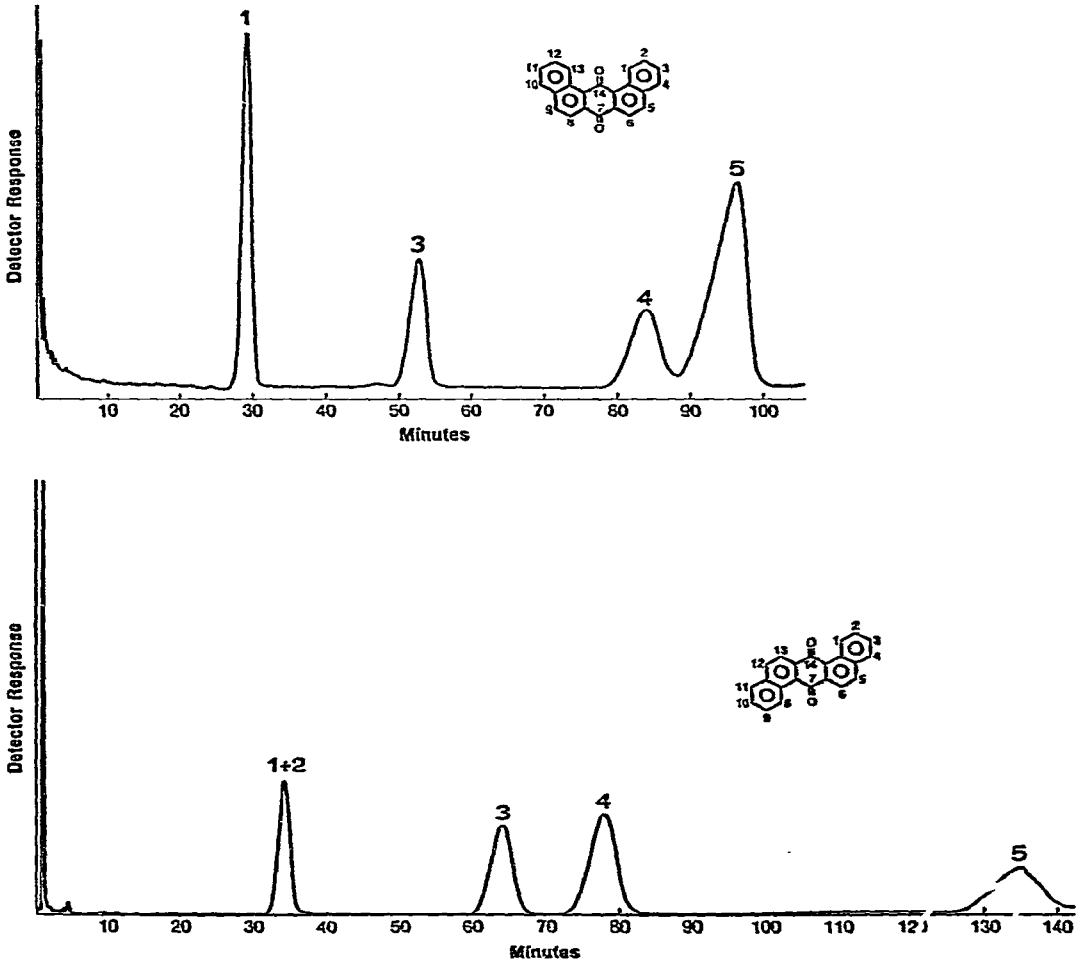


Fig. 3. Chromatograms of monomethoxydibenz[*a,h*] and [*a,j*]anthraquinones. Column: 3 ft. × 2 mm I.D.; packing: 2.5% BPhBT. Conditions: oven 262°C; flow-rate 60 ml/min. Peaks: 1 = unsubstituted; 2 = 1-CH_3O-; 3 = 2-CH_3O-; 4 = 4-CH_3O-; 5 = 3-CH_3O-.

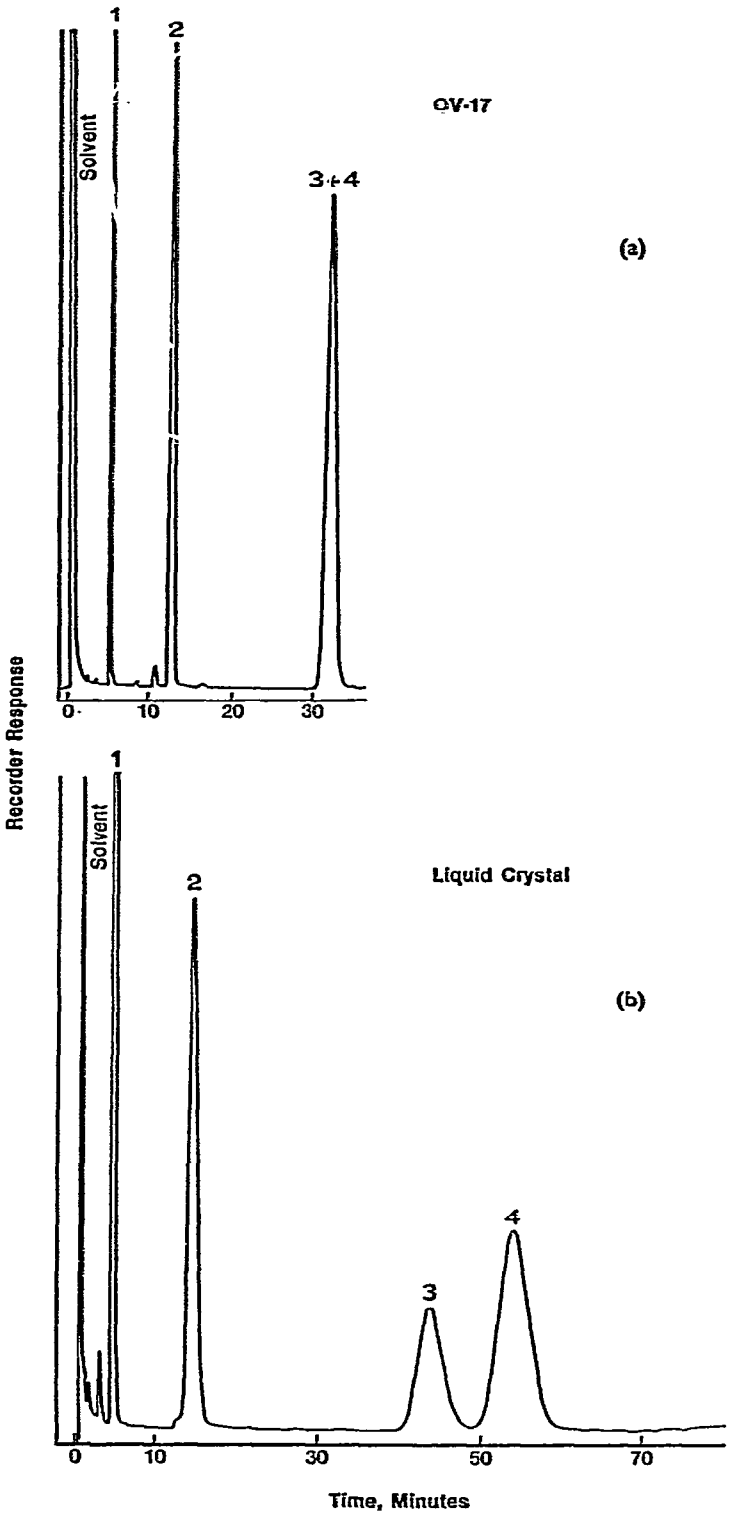


Fig. 4. Chromatograms of mono- and dimethoxyanthraquinones. (a) Column: 6 ft. × 2 mm I.D.; packing: 5% OV-17. Conditions: oven 262°C; flow-rate 60 ml/min. (b) Column: 6 ft. × 2 mm I.D.; packing: 2.5% BBBT. Conditions: oven 225°C; flow-rate 60 ml/min. Peaks: 1 = 9,10-ATQ; 2 = 2-CH_3O-ATQ; 3 = 2,7-diCH_3O-ATQ; 4 = 2,6-diCH_3O-ATQ.

with 1.00/1.10/1.34/1.28 using OV-17. The respective resolutions were $R_{1,2} = 6$; $R_{2,3} = 5$; $R_{3,4} = 6$ for the CH_3O-BATQ on BPhBT, superior to the resolutions obtained with OV-17. The retention ratios for the 5-, 6-, 7-, and 8-CH_3O-PhTQ were 1.00/2.33/3.54/2.60 using BBBT *versus* 1.00/1.00/1.29/1.24 using OV-17. The same improvement in the retention ratio and resolution was also noted for the CH_3O-DBATQ isomers (Table 1 and Fig. 3). Some of the mono- and dimethoxyquinones, which were not resolved on the OV-17 column, were easily resolved on the BBBT and BPhBT columns. The 5- and 6-CH_3O-PhTQ retention ratio on OV-17 was 1.00/1.00, but on BBBT it was 1.00/2.33 with a resolution of 3. Likewise, 2,7-diCH_3O-ATQ and 2,6- diCH_3O-ATQ were not resolved on OV-17 but were resolved with a retention ratio of 1.00/1.24 on BBBT as shown in Fig. 4. The DB[*a,h*]ATQ and DB[*a,j*]ATQ and their positional isomers (*e.g.* 2-CH_3O-DB[*a,j*]ATQ and 2-CH_3O-DB[*a,h*]ATQ) were not separated on OV-17. However, these compounds were easily separated on the liquid crystal columns (Fig. 4) with a retention ratio of 1.00/1.67 for the unsubstituted quinones with a resolution of 3.1.

An additional advantage of liquid crystal compared with OV-17 columns is the shorter elution time. For example, 3-CH_3O-BATQ eluted from BPhBT in 13.02 min *versus* 24.95 min from the OV-17 column. A disadvantage of the BBBT column was the tailing and non-Gaussian peaks observed for the terminal quinones, *e.g.* 1,4-NTQ, 6-CH_3O-NTQ, and 5-CH_3O-NTQ and the 1,4-PhTQ isomers. This was not observed using the OV-17 column. The peak shapes for the internal quinones using the liquid crystal columns were Gaussian as shown in Figs. 2–4.

The isomers with the larger length-to-breath ratios were consistently retained longer on the liquid crystal columns. These columns gave the best separations with the shortest elution times and were consistently better able to separate the closely related isomers. These results enabled us to assign tentative structures to isomers obtained from synthesis reactions from which two isomers were possible due to molecular symmetry or bond rotation. For example, the 1-CH_3O-BATQ and 3-CH_3O-BATQ were obtained from the reaction of naphthoquinone with *meta*-methoxystyrene. The ratio (10:1) of these two isomers in the isolated product mixture[1] was determined and tentative structures were assigned based on the data from the BPhBT and BBBT columns. The resolution of these two isomers was 17 using the BPhBT column. A mixture containing a 10:1 isomer ratio was easily integrated when $R = 17$. The detection, isomer identification, and relative amounts of 2,6- and 2,7-dimethoxyphenanthracene-9,10-diones, from the reaction of 6-methoxynaphthoquinone and 1-methoxy-3-trimethylsilyloxybutadiene, were also determined[6] using the BBBT column (Fig. 3). These columns have also been useful for the detection and quantitation of other isomeric products from synthetic reactions which could not be resolved by thin-layer chromatography or conventional GLC. The liquid crystal columns showed consistent separations based on length-to-breadth ratios which hold promise for predicting molecular structure of closely related isomers.

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