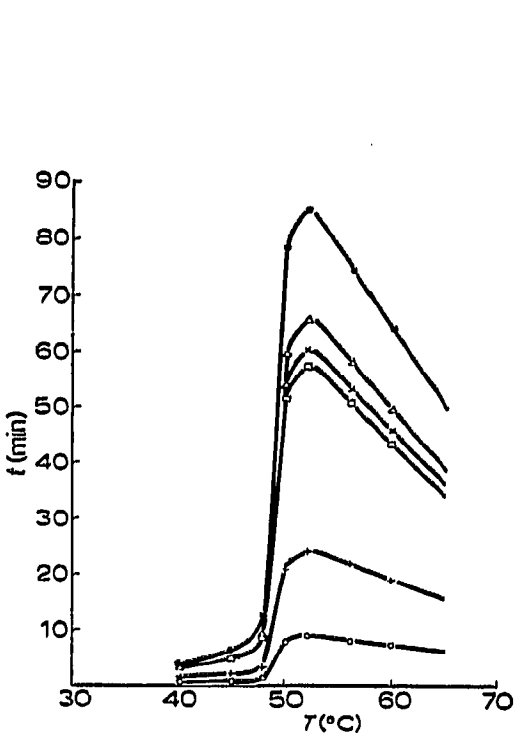
Behaviour of 7,8-benzoquinoline as stationary phase in gas–liquid chromatography in the vicinity of the melting point*

7,8-Benzoquinoline has been found[1] to be a good stationary phase for the separation of *p*- and *m*-xylene. However, we have noticed great differences in retention times depending on whether the equilibrium temperature of the column has been approached from a lower or higher temperature. The experimental data obtained with two different instruments are collected in Tables I and II and plotted in Figs. 1 and 2. They were perfectly reproducible provided that the conditions of the heating were the same. Since the largest differences appear in the vicinity of the melting point, but slightly below it, we have investigated by various physical methods the behaviour of 7,8-benzoquinoline near this temperature. First of all, the melting point was checked. The literature values are 52, 51 and 50°[2], but we have observed that a highly purified



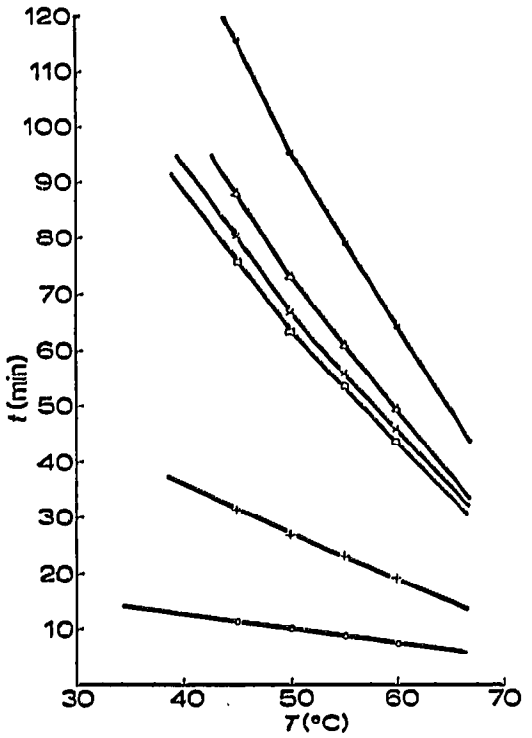


Fig. 1. Relative retention times as a function of increasing column temperature. (O) Benzene; (+) toluene; (□) ethylbenzene; (×) *p*-xylene; (△) *m*-xylene; (●) *o*-xylene.

Fig. 2. Relative retention times as a function of decreasing column temperature. (O) Benzene; (+) toluene; (□) ethylbenzene; (×) *p*-xylene; (△) *m*-xylene; (●) *o*-xylene.

sample actually shows pre-melting at 47° and the complete melting sets in at 52°. The substance regularly becomes undercooled and the crystallisation does not set in before 35°.

Differential thermal analysis shows (Fig. 3) three endothermal transitions with estimated temperatures 47, 52 and 55°. The n.m.r. spectrum is very instructive (Fig. 4). The relative intensity of the central line shows an increase from 47 to 50° with a possible inflection near 47°.

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TABLE I

RELATIVE RETENTION TIMES WITH INCREASING COLUMN TEMPERATURE

Column temperature (°C)	*40*		*45*		*48*		*50*		*52*		*55*		*60*	
Instrument	*Pye*	*PE 800*	*Pye*	*PE 800*	*Pye*	*PE 800*	*Pye*	*PE 800*	*Pye*	*PE 800*	*Pye*	*PE 800*	*Pye*	*PE 800*
Retention of benzene (min)	*0.79*	*1.89*	*0.95*	*3.00*	*1.42*	—	*7.90*	*8.53*	*9.00*	—	*8.21*	*7.27*	*7.42*	*6.16*
Benzene	1.00	1.00	1.00	1.00	1.00	—	1.00	1.00	1.00	—	1.00	1.00	1.00	1.00
Toluene	1.80	1.92	2.17	2.32	2.34	—	2.66	2.52	2.68	—	2.66	2.44	2.57	2.38
Ethylbenzene	4.00	4.08	5.34	6.48	6.11	—	6.52	5.84	6.36	—	6.17	5.45	5.87	5.25
p-Xylene		4.75				—	6.82	6.19	6.72	—	6.48	5.78	6.20	5.56
m-Xylene				7.00	6.56	—	7.58	6.69	7.30	—	7.04	6.24	6.68	6.00
o-Xylene	5.20	6.25	7.00	9.11	8.79	—	9.96	8.64	9.51	—	9.14	8.09	8.66	7.75

TABLE II

RELATIVE RETENTION TIMES WITH DECREASING TEMPERATURE

Column temperature (°C)	*60*		*55*		*50*		*45*		*40*	
Instrument	*Pye*	*PE 800*	*Pye*	*PE 800*	*Pye*	*PE 800*	*Pye*	*PE 800*	*Pye*	*PE 800*
Retention of benzene (min)	*7.42*	*6.48*	*8.68*	*7.58*	*9.94*	*8.68*	*11.21*	*10.26*	*12.95*	—
Benzene	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	—
Toluene	2.57	2.34	2.64	2.44	2.68	2.56	2.79	2.65	2.80	—
Ethylbenzene	5.87	5.12	6.15	5.54	6.38	5.90	6.79	6.26	6.30	—
p-Xylene	6.20	5.44	6.44	5.90	6.73	6.27	7.16	6.66	6.64	—
m-Xylene	6.68	5.85	7.02	6.36	7.35	6.84	7.86	7.26	7.36	—
o-Xylene	8.66	7.54	9.11	8.25	9.59	8.86	10.31	9.44	9.90	—

The results indicate that the transition of 7,8-benzoquinoline from solid to liquid goes through liquid crystal states. Similar phenomena were observed by BARRALL *et al.*[3] in the case of cholesteryl esters and by KELKER[4], DEWAR AND SCHROEDER[5,6] and other authors in the case of *p*-azoxy, *p*-alkoxy and similar compounds. Our results suggest that the good separating properties of 7,8-benzoquinoline for xylenes are due to its mesomorphic structure.

Experimental

7,8-Benzoquinoline samples from two sources were investigated: BDH Laboratory Reagent and Perkin Elmer column packing material (part. No. 154-0752).

Pye Argon Chromatograph and Perkin Elmer Model 800 instruments were used.

Experimental conditions for the Pye Argon Chromatograph.

Column packing: Embacel, 60–100 mesh, acid washed, with 25% 7,8-benzoquinoline

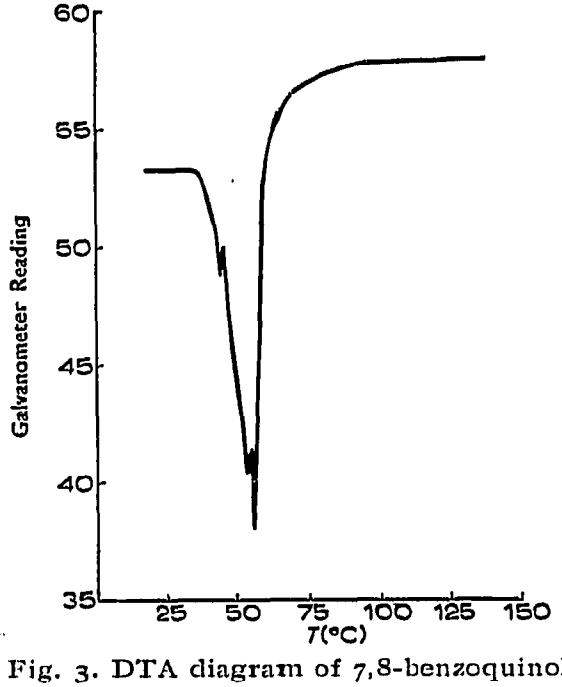

Fig. 3. DTA diagram of 7,8-benzoquinoline.

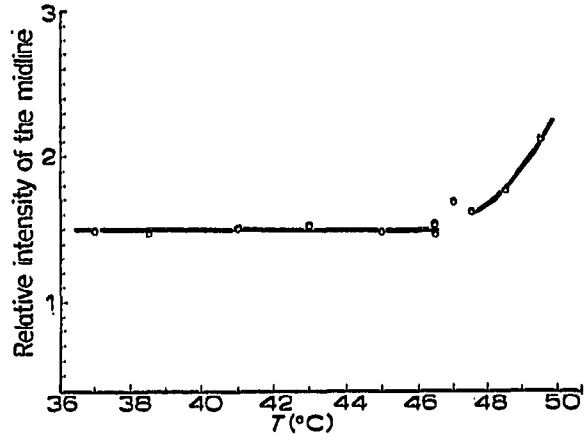

Fig. 4. The relative intensity of the central line in n.m.r. spectrum as a function of temperature.

Column diameter and length: 0.4 cm, 118 cm
Weight of column packing: 8.4 g
Column temperature: 40 to 60° ± 2°
Carrier gas: argon
Carrier gas flow: 50 ml/min; inlet pressure: 0.21 to 0.27 atm
Sensitivity: 10 ×
Detector voltage: 1500 V

Experimental conditions for the Perkin Elmer Model 800 Chromatograph.
Column packing: PE column X
Column diameter and length: 0.32 cm, 366 cm
Column temperature: 40 to 60° ± 2°
Carrier gas: argon
Carrier gas flow: 24 ml/min; inlet pressure: 2 atm
Detector: FID
Air pressure: 2.5 atm, hydrogen pressure: 1.0 atm
Attenuation: 500 and 1000

The melting points were determined with Kofler's polarizing melting microscope with a heating programme 2°/min. The errors of results were ± 1°.

An adapted differential thermal analysis instrument, with a heating programme 3°/min, and Al_2O_3 as reference material was used. The accuracy of temperature data was ± 2°.

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1 D. H. DESTY, A. GOLDUP AND W. T. SWANTON, *Nature*, 183 (1959) 107.
2 *Beilstein's Handbuch der organischen Chemie, Vol. XX*, pp. 458, 463, 464.
3 E. M. BARRALL, R. S. PORTER AND J. F. JOHNSON; *J. Chromatog.*, 21 (1966) 392.
4 H. KELKER, *Z. Anal. Chem.*, 198 (1963) 254.
5 M. J. S. DEWAR AND J. P. SCHROEDER, *J. Am. Chem. Soc.*, 86 (1964) 5235.
6 M. J. S. DEWAR AND J. P. SCHROEDER, *J. Org. Chem.*, 30 (1965) 3485.

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