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Resorcarene derivative used as a new stationary phase for capillary gas chromatography

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Abstract

Resorcarene derivative, 2,8,14,20-tetraphenyl-4,6,10,12,16,18,22,24-octapentyloxy-pentacyclo-[19.3.1.^{3,7}.1^{9,13}.1^{5,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecene (phenyl-pentyloxy-resorcarene) was synthesized and used as a new stationary phase for capillary gas chromatography. The results showed that it had high column efficiency, medium polarity and excellent selectivity, especially for the separation of substituted benzenes. In the separation, strong retention ability for naphthalene and its analogs was observed. The thermal stability of this new stationary phase was also tested.

Keywords: Stationary phases, GC; Resorcarene stationary phases; Phenylpentyloxyresorcarene stationary phases; Benzenes

1. Introduction

Crown ethers and cyclodextrins have been widely used as gas chromatography (GC) stationary phases in recent years. Because of their cavity structure, they are good host compounds and can form inclusion compounds with a wide range of guest molecules [1–5].

Resorcarenes and calixarenes are also host compounds with cavity structures. Resorcarenes are composed of four alkylidene-bridged resorcinol units (Fig. 1a), while the calixarenes are cyclic phenol–formaldehyde polycondensates (Fig. 1b). Their residues R and OH can be modified for GC purposes. As host compounds, they have essential merits for their employment as GC stationary phases.

Some calixarenes have been used as GC stationary phases for isomer separation. *p-tert.*-Butylcalix[4]arene was first used as a packed GC stationary phase by Smolkova-Keulemansova and Feltl [6] and Mangia et al. [7] used *p-tert.*-butylcalix[8]arene as a stationary phase in gas–solid chromatography (GSC) and studied its retention behaviour for alkanols, chlorinated hydrocarbons and aromatic compounds. In 1992, Mckervey and Bohmer [8] reviewed the properties and applications of calixarene. Glennon et al. [9] used silica bonded calix[4]arene tetraester as a liquid chromatography (LC) stationary phase. Recently, Mnuk and coworkers studied the inclusion properties of *p-tert.*-butylcalix[4]arene in GSC [10] and in capillary GC [11]. Several papers have studied the synthesis [12–14] and host–guest interactions [15] of resorcarenes and their use as pseudo-stationary phases in electrokinetic chromatography (EKC) has been reported by Bachmann et al. [16]. Currently, the application of resorcarenes to GC has not yet been reported.

In this paper, we synthesized a resorcarene deriva-

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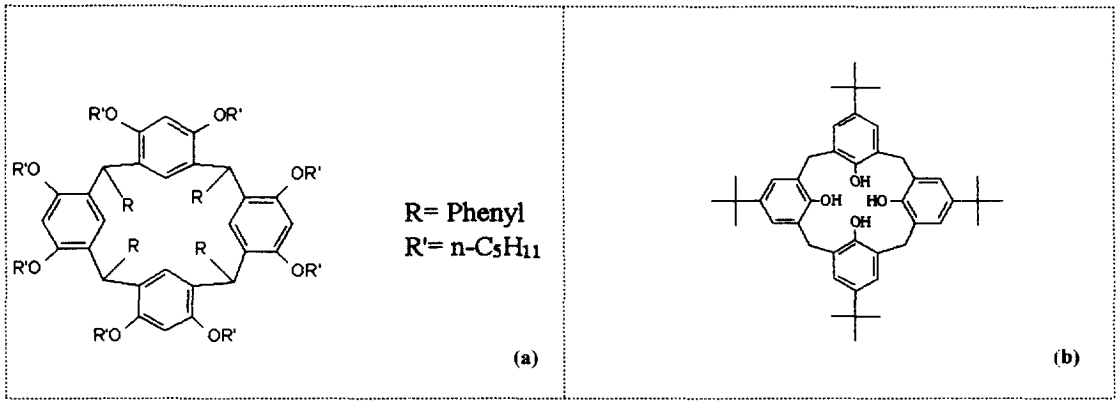


Fig. 1. (a) The structure of phenyl-pentyloxy-resorcarene stationary phase. (b) The structure of calixarene.

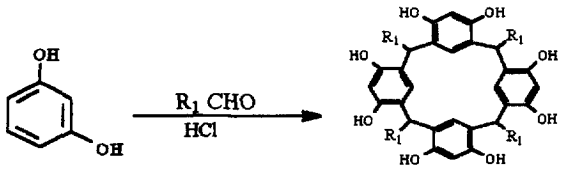
tive, 2,8, 14, 20-tetraphenyl-4,6,10,12,16,18,22,24-octapentyloxy-pentacyclo-[19.3.1.^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3, 5, 7(28),9, 11, 13(27), 15, 17, 19(26), 21, 23-dodecene (phenyl-pentyloxy-resorcarene) and successfully coated this derivative onto fused-silica capillary columns. The chromatographic characteristics of this new stationary phase were studied and some unique properties were observed in GC separation.

2. Experimental

2.1. Syntheses

2.1.1. Synthesis of 2,8,14,20-tetraphenylpentacyclo-[19.3.1.^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecene-4,6,10,12,16,18,22,24-octol (phenyl-hydroxy-resorcarene)

According to the reaction:

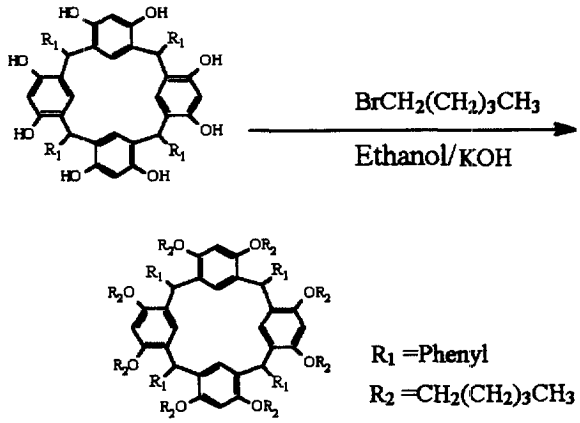


R$_1$=Phenyl

10.6 g (0.1 mol) of benzaldehyde was added into a stirred solution of 11.0 g (0.1 mol) of resorcinol in 60 ml of ethanol and 20 ml of concentrated hydrochloric acid at 5°C (dropwise over 1 h). The solution was refluxed for 8 h and then cooled to room temperature. A gummy precipitate formed, which crystallized when water was added. After filtrating, washing with water and recrystallizing from acetone, pure phenyl-hydroxy-resorcarene was obtained.

2.1.2. Synthesis of phenyl-pentyloxy-resorcarene

According to the reaction:



4.4 ml (0.035 mol) of 1-bromopentane was added to a stirred solution of 2.4 g (0.004 mol) of phenyl-hydroxy-resorcarene and 2.0 g (0.035 mol) of KOH in 70 ml of ethanol. The solution was refluxed for 2.5 h and then cooled to room temperature. When the solid was filtrated and the ethanol was evaporated, a glassy solid was obtained, which was purified by column chromatography [15×5 cm, silica gel, di-

chloromethane–light petroleum (boiling range, 60-90°C) (1:4)].

IR($\bar{v}$, cm^{-1}): 3030, 2930, 2850, 1610, 1580, 1500, 1300, 1190.

^1H NMR (90 Hz, C^2HDCl_3, δ ppm, TMS): 7.40–6.95(m, 28H, Ar*H*), 3.90(m, 4H, Ar*H*Ar), 3.40–3.00(m, 16H, $OCH_2(CH_2)_3CH_3$), 2.40–2.00(m, 16H, $OCH_2CH_2(CH_2)_2CH_3$), 1.30–0.98(m, 32H, $OCH_2CH_2(CH_2)_2CH_3$), 0.90–0.56(m, 24H, CH_3).

2.2. TGA and DTA tests

In order to evaluate the thermal stability of phenyl-pentyloxy-resorcarene, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) tests were carried out on an LCT-2 TGA analysis instrument (Beijing Optical Instrument Factory, Beijing, China). The sample weight was 10 mg and the operating temperature range was from 25°C to 600°C at rate of 15°C/min. The TGA and DTA curves are shown in Fig. 2. It can be clearly seen that the sample began to decompose slightly at 240°C and dramatically between 300°C–370°C. It means that this new stationary phase is thermostable below 240°C and suitable for GC use.

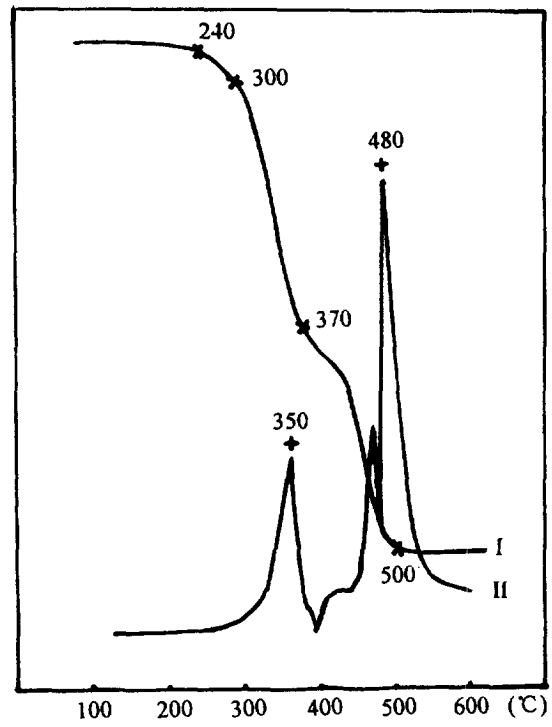


Fig. 2. TGA and DTA curves for phenyl-pentyloxy-resorcarene. Curve 1: TGA; curve 2: DTA.

2.3. Column preparation

Fused-silica capillary tubing (0.25 mm I.D., Yong Nian Optical Fibre Factory, Hebei, China) was treated by depositing sodium chloride onto the inner wall of column [17]. Then the columns were statically coated with a solution of 0.50% (w/v) of phenyl-pentyloxy-resorcarene stationary phase in dichloromethane at 35°C, the film thickness is approximately 0.31 μm. Following coating and flushing with nitrogen for 2 h, the columns were conditioned at 100°C, 120°C, 140°C, 160°C, 180°C and 200°C for 2 h each and finally at 220°C for 6 h.

2.4. Column evaluation

The GC separations were carried out on a SP-3700 gas chromatograph (Beijing Analytical Instrument Factory, Beijing, China) equipped with a flame ionization detection (FID) system. Carrier gas was nitrogen. The output of the detector was connected to a LDC/Milton Roy CI-10 integrator and Hitachi 561 recorder. The injection split ratio was (80:1). The injector and detector temperatures were 260°C and 280°C, respectively. All samples were reagent grade.

3. Results and discussion

3.1. Column efficiency

Table 1 lists the characteristics of the three capillary columns coated with phenyl-pentyloxy-resorcarene. Three compounds, dodecan (non-polar), naphthalene (medium-polar) and nonanol (high-polar), were used to evaluate column efficiency, respectively. The columns possess high efficiency and fine reproducibility. Although naphthalene and nonanol have nearly the same boiling points, the retention value of naphthalene is larger than that of nonanol at the same column temperature as shown in Table 1. It is considered that the strong retention

Table 1
Chromatographic properties of the phenyl-pentyloxy-resorcarene columns

No.	Dimension (m×mm)	Film thickness (μm)	Flow-rate (cm/s)	Dodecane (temperature 120°C)		Naphthalene (temperature 140°C)		Nonanol (temperature 140°C)	
				k	N	k	N	k	N
1	12.2×0.25	0.31	14.5	3.13	3660	4.54	4130	2.63	3220
2	18.7×0.25	0.31	14.5	3.13	3680	4.69	3840	2.78	3930
3	21.5×0.25	0.31	14.3	3.33	2890	4.81	3260	2.77	3730

k: Capacity factor.
N: Theoretical plate number.

ability to naphthalene is due to the inclusion interaction with the cavity of phenyl-pentyloxy-resorcarene.

3.2. Polarity

The polarity of the phenyl-pentyloxy-resorcarene stationary phase was represented by McReynolds' constant (ΔI) at 120°C. Table 2 shows that the polarity of this new stationary phase is medium. The elution sequences of the McReynolds' probes are X′→Y′→Z′→U′→S′.

3.3. Grob test

Grob test mixtures were used to evaluate the overall characteristics of the capillary column. Fig. 3 shows the chromatogram of Grob test mixtures on column 3. All components of Grob are well separated and produce nearly symmetrical peaks. It should be noted that naphthalene is eluted after tridecane and 2,4-dimethylaniline (2,4-DMA), showing that this resorcarene stationary phase has special retention ability for naphthalene. It is possible that the host–guest interaction will take place during the separation process. It should also be noted that 2,6-dimethylphenol (2,6-DMP) elutes before 2,4-DMA. It means that hydrogen bonding is not an influential factor in this separation course. The peak of 1-octanol is nearly symmetrical, showing that this stationary phase has a good film formation ability.

3.4. Separation of some isomers

This phenyl-pentyloxy-resorcarene stationary phase has unique selectivity for the separation of position isomers. Table 3 shows the separation factors (α) and capacity factors (k) for the compounds investigated. The chlorotoluene isomers are separated excellently as shown in Fig. 4. It is noted that the separation factor of p- and m- chlorotoluenes [similar boiling points (b.p.s)] is larger than that of m- and o-chlorotoluenes (difference of b.p. = 2.9°C), $\alpha_{p/m}$ is 1.06 and $\alpha_{m/o}$ is 1.05. The cresol isomers are also well separated on this stationary phase (Fig. 5), the separation factors (α) of m- (b.p. 202.2°C) and p-cresols (b.p. 201.9°C) are up to 1.03.

Although the boiling points of m- and p-chlorotoluenes are nearly similar (b.p. 162°C), their dipole moments are obviously different (dipole moment: $m = 1.92$, $p = 2.21$). The elution order of m- and p-chlorotoluenes is $m \rightarrow p$. That is in agreement with their dipole–dipole force sequence. It means that the dipole–dipole force has an obvious effect on chlorotoluene isomer separation. From Table 3, m- and p-isomers of xylenes, dibromobenzenes and dichlorobenzenes cannot be separated or just slightly separated, while m- and p-isomers of chlorotoluene

Table 2
McReynolds' constants of the phenyl-pentyloxy-resorcarene stationary phase

Stationary phase		X′	Y′	Z′	U′	S′	Average
Phenyl-pentyloxy-resorcarene	I	766	773	807	890	954	
	ΔI	113	146	217	191	302	194

X′: Benzene; Y′: 1-butanol; Z′: 2-pentanone; U′: nitropropane; S′: pyridine.

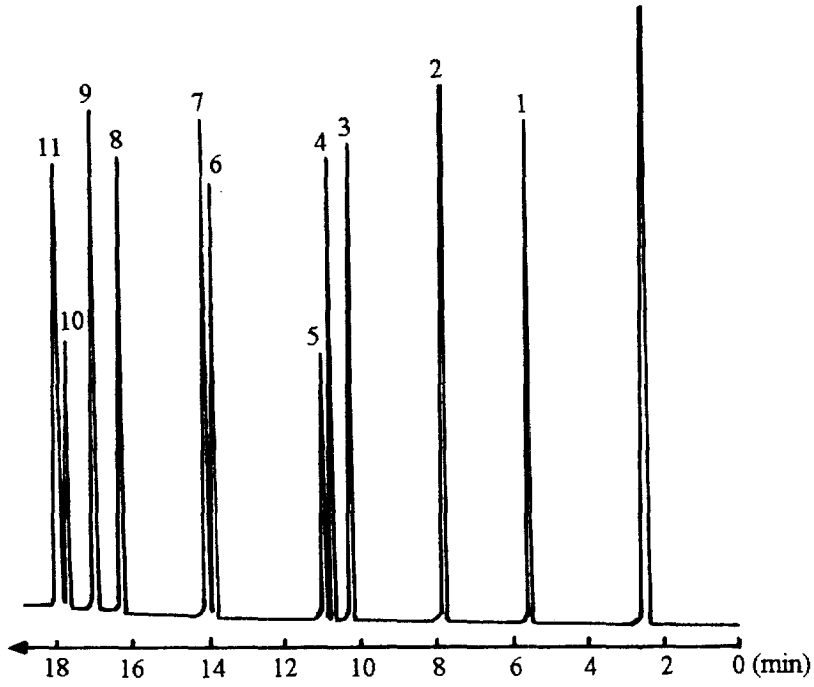


Fig. 3. Chromatogram of Grob test mixture on column 3. Column heating: 100°C to 160°C (10 min) at 4°C/min. N_2 linear veleocity: 14.3 cm/s. Peaks: 1 = *n*-decane; 2 = *n*-undecane; 3 = 1-octanol; 4 = *n*-dodecane; 5 = nonaldehyde; 6 = 2,6-dimethylphenol; 7 = *n*-tridecane; 8 = 2,4-dimethylaniline; 9 = naphthalene; 10 = methyl decanoate; 11 = tetradecane.

and bromotoluene can be easily separated. It can also be considered that the same substituted group at the *m*-, *p*-position will cause little structure configuration difference compared with different substituted groups at the *m*-, *p*-position on these disubstituted benzenes. Furthermore, Table 3 also shows an interesting separation phenomenon: the elution order of *m*- and *p*-isomers of nitrochlorobenzene and dimethoxybenzene on this stationary phase was against their b.p. order. This is due to the special inclusion interactions of host–guest molecules. On the other hand, for bromotoluene, dichlorobenzene, nitrotoluene, nitrobromobenzene and cresol, these isomers elution orders are in agreement with boiling point.

3.5. Selectivity

Fig. 6 shows that benzene (b.p. = 80.1°C), cyclohexane (b.p. = 80.7°C) and *n*-hexane (b.p. = 69.0°C) can be completely separated on phenyl-pentyloxy-resorcarene stationary phase. These compounds can not be separated successfully on a micropacked column of *p-tert.*-butylcalix[4]arene [10]. Figs. 7 and 8 show the chromatograms of xylenol and dimethylnaphthalene isomers, respectively. Xylenol isomers are separated completely ($\alpha_{2,4/2,5} = 1.03$, $\alpha_{2,3/3,4} = 1.04$). Dimethylnaphthalene (DMN) isomers are partially separated at 180°C. 1,4- and 2,3-DMN are eluted at same time, others are well separated. This resorcarene derivative has a strong retention ability for naphthalene analogs, caused by its possible bicyclic high electrophoretic mobility on the host molecule (see Fig. 9).

3.6. Column bleeding test

To determine the maximum operating temperature of phenyl-pentyloxy-resorcarene column, column bleeding was measured by programming the operating temperature from 160°C to 300°C at 4°C/min. The baseline begins to drift dramatically at 240°C, which means that the bleeding temperature was

Table 3
Capacity factor (k) and relative retention (α) of tested compounds on column 3

Compound tested		Boiling point (°C, 760 mmHg)	Capacity ratio (k)	Relative retention (α)	Temperature (°C)
Xylene	*o*-	144.4	3.17	1.29	80
	m-	139.1	2.46	1.00	
	p-	138.3	2.46	1.00	
Chlorotoluene	*o*-	159.1	2.90	1.00	100
	m-	162	3.04	1.05	
	p-	162	3.21	1.11	
Bromotoluene	*o*-	181.7	2.96	1.00	120
	m-	183.7	3.08	1.04	
	p-	184.3	3.23	1.09	
Dichlorobenzene	*o*-	180.5	3.71	1.37	120
	m-	173	2.71	1.00	
	p-	174	2.75	1.02	
Dibromobenzene	*o*-	225	6.38	1.29	140
	m-	218	4.96	1.00	
	p-	218~219	4.96	1.00	
Nitrotoluene	*o*-	221.7	1.65	1.00	180
	m-	232.6	2.07	1.25	
	p-	238.3	2.42	1.46	
Nitrochlorobenzene	*o*-	246	4.13	1.29	170
	m-	235~236	3.29	1.03	
	p-	242	3.19	1.00	
Nitrobromobenzene	*o*-	258 (756 mmHg)	5.33	1.23	180
	m-	265	4.46	1.03	
	p-	256	4.33	1.00	
Dimethoxybenzene	*o*-	206 (759 mmHg)	5.21	1.00	130
	m-	217~218	5.60	1.08	
	p-	212.6	5.75	1.10	
Toluidine	*o*-	200.2	3.54	1.00	130
	m-	203.3	3.75	1.06	
	p-	200.5	3.54	1.00	
Cresol	*o*-	191	3.63	1.00	130
	m-	202.2	4.67	1.29	
	p-	201.9	4.58	1.26	
Naphthalene			1.54	1.00	180
1-Methylnaphthalene		244.64	2.75	1.78	
2-Methylnaphthalene		241.05	2.50	1.62	

Taken from Ref. [18].
1 mmHg = 133.322 Pa.

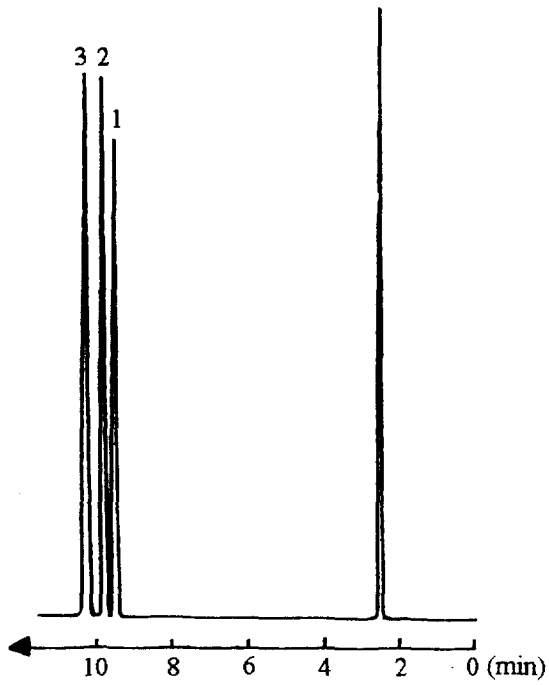


Fig. 4. Chromatogram of chlorotoluene on column 3 at 100°C. N_2 linear veleocity: 14.3 cm/s. Peaks: 1 = *o*-chlorotoluene; 2 = *m*-chlorotoluene; 3 = *p*-chlorotoluene.

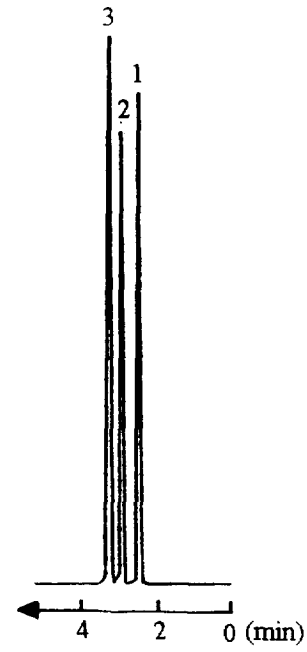


Fig. 6. Chromatogram of benzene, cyclohexane and hexane on column 3 at 80°C. N_2 linear veleocity: 14.3 cm/s. Peaks: 1 = hexane; 2 = cyclohexane; 3 = benzene.

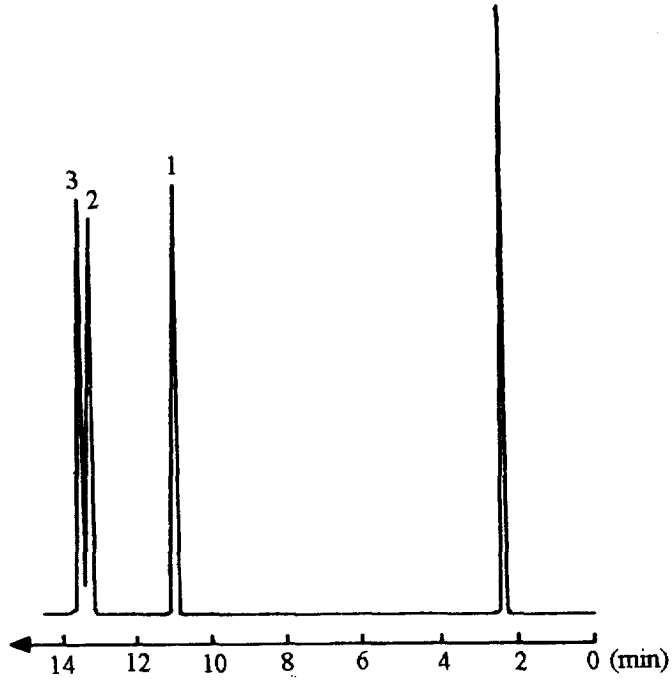


Fig. 5. Chromatogram of cresol on column 3 at 120°C. N_2 linear veleocity: 14.3 cm/s. Peaks: 1 = *o*-cresol; 2 = *p*-cresol; 3 = *m*-cresol.

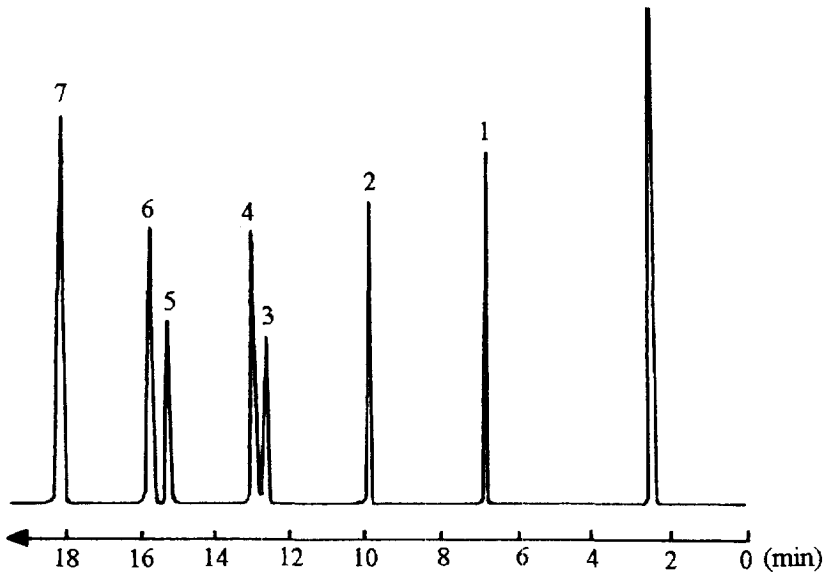


Fig. 7. Chromatogram of xylenol isomers and phenol on column 3 at 140°C. N_2 linear veleocity: 14.3 cm/s. Peaks: 1 = phenol; 2 = 2,6-xylenol; 3 = 2,5-xylenol; 4 = 2,4-xylenol; 5 = 3,5-xylenol; 6 = 2,3-xylenol; 7 = 3,4-xylenol.

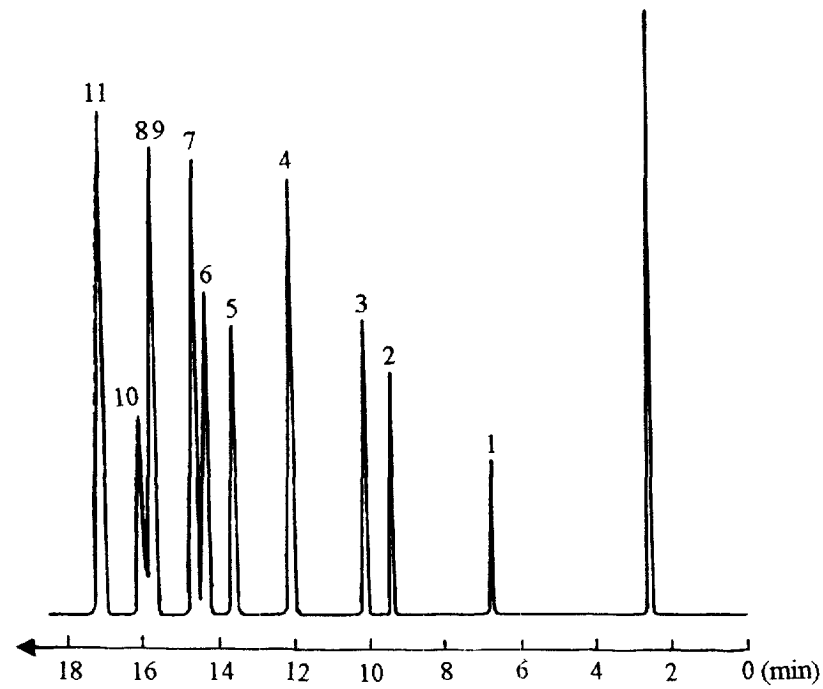


Fig. 8. Chromatogram of naphthalene and its analogs on column 3 at 180°C. N_2 carrier linear veleocity: 14.3 cm/s. Peaks: 1 = naphthalene; 2 = 2-methylnaphthalene; 3 = 1-methylnaphthalene; 4 = biphenyl; 5 = 2,6-dimethylnaphthalene (DMN); 6 = 1,7-DMN; 7 = 1,6-DMN; 8,9 = 1,4- and 2,3-DMN; 10 = 1,5-DMN; 11 = 1,2-DMN.

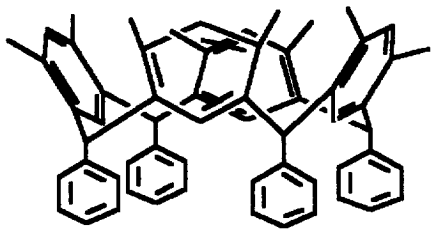


Fig. 9. Possible bibicycle structure of the phenyl-pentyloxy-resorcarene stationary phase.

240°C; this is in agreement with the data of the TGA and DTA tests.

4. Conclusions

The resorcarene derivative (phenyl-pentyloxy-resorcarene) has good thermal stability below 240°C. It shows a good film-formation ability and possesses high efficiency as a special stationary phase for high-resolution gas chromatography. Alkanes, alkanols, phenols and aromatic hydrocarbons are well separated on this new stationary phase, especially chlorotoluene, cresol and xylenol isomers. This stationary phase has special retention ability for naphthalene and its analogs.

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