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Gas chromatographic study of the inclusion properties of calixarenes

I. *p*-*tert*-Butylcalix[4]arene in a micropacked column

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Abstract

Quantitative structure–retention relationships (QSRR) in gas–solid chromatography (GSC) were employed as an auxiliary method to study the inclusion properties of *p*-*tert*-butylcalix[4]arene. Selected experimental retention data were studied thermodynamically. The sorbates involved homologous series of aliphatic and alicyclic alkanes and alkenes, aromatics, halo derivatives, alcohols and ethers. It is presumed that *p*-*tert*-butylcalix[4]arene forms inclusion complexes with benzene, its lower *n*-alkyl derivatives (toluene to *n*-butylbenzene), *p*-dialkylbenzenes (*p*-xylene, *p*-ethyltoluene), *m*-xylene, di- and trichloromethane, methanol and ethanol under GSC conditions.

1. Introduction

Calixarenes, i.e., cyclic phenol–formaldehyde polycondensates (Fig. 1), are capable of selective interactions with many metal ions and organic molecules. X-ray structural analysis and ¹H NMR spectroscopy have demonstrated that *p*-

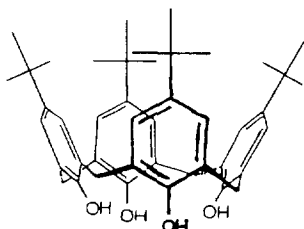


Fig. 1. The most stable conformation (cone) of *p*-*tert*-butylcalix[4]arene (schematic).

tert-butylcalix[4]arene forms inclusion complexes with benzene [1], toluene [2], *p*-xylene [1], phenol [3], anisole [1,4] and chloroform [5]. There also exist complexes of *p*-*tert*-butylcalix[4]arene derivatives with acetonitrile [6], pyridine [7] and ethanol [8], complexes of *p*-isopropylidihomooxalix[4]arene with *o*-xylene [9], *p*-*tert*-butyldihomooxalix[4]arene with 1,3,5-trimethylbenzene [10] and a complex of a bis-*p*-*tert*-butylcalix[4]arene derivative with dichloromethane [11].

Preparation of crystals suitable for X-ray structural analysis from a convenient solvent and ¹H NMR studies of calixarene complexes in solution bring about certain problems. Unsubstituted calixarenes are very poorly soluble in most organic solvents. The weak intermolecular interactions predominating in molecular complexes of calixarenes with neutral organic molecules are often insufficient for competitive displacement of

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solvent molecules from the calixarene cavity. The cavities in solvated calixarenes are not rigid and are subject to rapid processes leading to a conformational inversion of the molecule. In a mass spectrometric study of the formation of inclusion complexes in the gaseous phase, only a complex of *p*-*tert*-butylcalix[4]arene with benzene was demonstrated [12].

In this study we applied a non-traditional approach to study the inclusion properties of calixarenes, which is based on the low-temperature deposition of calixarenes on the surface of a suitable support. The structure of calixarene molecules is thus conformationally stabilized and is exposed to a stream of an inert carrier gas containing active low-molecular-mass components. The first experiments of this type were carried out in 1982 at Charles University in Prague [13] and at Parma University, Italy [14]. This relatively well defined system was used for the specification of group of substances that selectively interact with *p*-*tert*-butylcalix[4]arene under gas chromatographic conditions. On the basis of the retention behaviour of selected homologous series, we tried to characterize the kind of intermolecular interactions taking part in the gas chromatographic separation process. This is the first effort concerning the systematic investigation of the selectivity of calixarenes in gas chromatography.

2. Theoretical

The following non-specific interactions, described by their potential energies E , can be expected to occur in molecular complexes of the calixarene–electroneutral organic molecule type under gas–solid chromatographic (GSC) conditions:

Dispersion interactions:

$$E_d = -\left(\frac{1}{4\pi\epsilon_0}\right)^2 \cdot \frac{3}{2} \cdot \frac{I_1 I_2}{I_1 + I_2} \cdot \frac{\alpha_1 \alpha_2}{\epsilon r^6} \quad (1)$$

Dipole–dipole interactions:

$$E_{d-d} = -\left(\frac{1}{4\pi\epsilon_0}\right)^2 \cdot \frac{2}{3kT} \cdot \frac{\mu_1^2 \mu_2^2}{\epsilon r^6} \quad (2)$$

Dipole–induced dipole interactions:

$$E_{d-id} = -\left(\frac{1}{4\pi\epsilon_0}\right)^2 \cdot \frac{\alpha_1 \mu_2^2 + \alpha_2 \mu_1^2}{\epsilon r^6} \quad (3)$$

where I denotes the ionization energies of the interacting molecules, α their polarizabilities, ϵ the relative permittivity of the surroundings, r the distance between the interacting molecules, k the Boltzmann constant, T the absolute temperature and μ the dipole moments of the interacting molecules.

Among specific interactions, inclusion, induced fit, hydrogen bonding, electron pair donor–acceptor, electron pair repulsive interactions and entropic effects can be assumed. The terms T (constant column temperature) and $I_1 I_2 / (I_1 + I_2)$ in general, and the terms α and μ^2 for calixarene, in Eqs. 1–3 can be considered to be constant. The gas chromatographic retention data ($\log k$, $\log V_g$) can be considered to be directly proportional to the interaction energy between the sorbates and the stationary phase. Using the method of quantitative structure–retention relationship (QSRR [15]) it is thus possible to study, in congeneric series, the course of the sorbate–stationary phase dispersion interactions on the basis of retention data dependences on the analyte polarizabilities (α) and molar volumes (MV), and the course of electrostatic interactions from retention data dependences on the analyte dipole moments (μ) or the $\alpha + \mu^2$ values, provided that the required data are available. The effect of the sum of Van der Waals interactions can then be found from retention data dependences on the analyte boiling points (b.p.) or enthalpies of vaporization. The deviations from these standard dependences refer to the presence of certain specific interactions. For quantitative evaluation of these deviations in a congeneric series of sorbates, the quantity IRT_s^D has been defined by the equation

$$IRT_s^D = \frac{t'_{r,X} - t'_{r,H}}{t'_{r,H}} \cdot 100 \quad (4)$$

where D is a defined molecular descriptor and S a reference homologous series, $t'_{r,X}$ is the experimental adjusted retention time for sorbate X

and $t'_{r,H}$ is a calculated adjusted retention time obtained by regression analysis for a hypothetical sorbate that elutes in agreement with the given homologous series and whose physico-chemical data are identical with those of sorbate X. The quantity IRT_s^D can be handled in the same way as retention data.

Thermodynamic data are calculated using the equations

$$\Delta G^0 = -RT \ln K \quad (5)$$

$$K = V_g \cdot \frac{M}{T_0 R} \quad (6)$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (7)$$

where K is the distribution coefficient, V_g the specific retention volume, M the molar mass of the stationary phase (calixarene) and T the column absolute temperature. It follows from Eqs. 5–7 that

$$\log V_g = -\frac{\Delta H^0}{2.3R} \cdot \frac{1}{T_c} + \frac{\Delta S^0}{2.3R} - \log\left(\frac{M}{T_0 R}\right) \quad (8)$$

The $\log V_g$ vs. $1/T_c$ dependence permits the determination of the mean differential molar enthalpy for the sorbate–stationary phase interaction, ΔH^0 , and an estimation of the mean differential molar entropy, ΔS^0 , of the process. The mean differential Gibbs energy, ΔG^0 , can be found from Eqs. 5 and 6 for a given column temperature. Using the relationships valid between the activity coefficients and the ΔH^0 and ΔS^0 values under certain conditions [16], the above interactions can also be evaluated from so-called compensation graphs of enthalpy and entropy [17].

3. Experimental

The stationary phase was prepared by dissolving *p*-tert.-butylcalix[4]arene (Shinkai Chemirecognics Project, Japan) in dichloromethane (the solubility is 130 mg per 100 ml at 20°C), mixing the solution with silanized Chromosorb W (100–120 mesh) (Carlo Erba) and allowing the solvent to evaporate freely at atmospheric pres-

sure; the temperature was maintained below 23°C during the whole procedure. The thermal stability of the prepared phase was assessed from thermogravimetric analysis and a limiting temperature of 280°C was obtained. The stationary phase, containing 3.2% (w/w) of *p*-tert.-butylcalix[4]arene, was transferred into a glass micropacked column (1.64 m × 1 mm I.D.). A reference column (1.65 m × 1 mm I.D.), containing pure silanized Chromosorb W (100–120 mesh) (Carlo Erba), was prepared analogously. A reference column (0.62 m × 1 mm I.D.) was packed with silanized Porapak P (Waters). The structure of the cross-linked divinylbenzene–styrene copolymer represents the dense network of the aromatic (π -electron-donor) centres.

The stationary phase containing *p*-tert.-butylcalix[4]arene was conditioned at temperatures from 70 to 280°C for 120 h; the progress of the conditioning procedure was checked on the basis of the retention behaviour of cyclohexane, benzene, toluene, xylenes, methanol, ethanol and *n*-propanol.

The measurements were carried out on a Chrom 61 gas chromatograph with a flame ionization detector (Laboratorní Přístroje, Prague, Czech Republic), maintaining the thermostat temperature within $\pm 0.1^\circ\text{C}$ and the carrier gas flow-rate within $\pm 0.02 \text{ ml min}^{-1}$. The column temperature was varied from 50 to 130°C and the carrier gas (nitrogen) flow-rate from 7.5 to 20.0 ml min^{-1} . The retention times were measured with a Casio digital stop-watch with a precision of 0.01 s. The analytes were injected using the headspace method with Hamilton microsyringes; the vapour volume varied from 10 to 100 μl at 25°C.

4. Results and discussion

The formation of inclusion compounds of *p*-tert.-butylcalix[4]arene was studied with homologous series of aliphatic and alicyclic alkanes and alkenes, aromatics, alcohols, ethers and halogenated hydrocarbons. The retention behaviour of the homologous series on the reference Porapak P column indicates that dispersion inter-

actions predominate (even with alcohols, ethers and halo derivatives); specific π - π interactions complement dispersion interactions for aromatics. The homologous series are eluted within a relatively narrow time interval in the order alcohols < ethers < alkanes/alkenes < halo derivatives < aromatics. The retention behaviour on silanized Chromosorb W is affected by the residual OH active sites remaining after silanization. Hydrogen bonding predominates for alcohols, ethers and halo derivatives, whereas orientation dipole-dipole interactions are dominant for aromatics and alkenes. The microporous structure of the pure support probably also plays a role. The homologous series are eluted over a wide time interval, in the order alkanes < alkenes < aromatics, halo derivatives < ethers < alcohols. The retention behaviour of the homologous series on *p*-*tert*-butylcalix[4]arene indicates a strong influence of the phenolic hydroxyls in calixarene on the overall interaction mechanism for the sorbates. The homologous series are eluted over a wide time interval, the order being alkanes < alkenes < halo derivatives < aromatics < ethers < alcohols.

4.1. Retention behaviour of saturated and unsaturated aliphatic and alicyclic hydrocarbons

The retention data for lower (up to C_8) and higher (C_9 - C_{13}) *n*-alkanes and *n*-alkenes on the *p*-*tert*-butylcalix[4]arene column exhibit linear dependences on selected molecular descriptors, namely the boiling point (b.p.), molar volume (*MV*), polarizability (α) and enthalpy of vaporization. Electrokinetic dispersion interactions predominate. *p*-*tert*-Butylcalix[4]arene behaves selectively toward the π -electron systems in alkenes and cycloalkenes, depending on the position and number of double bonds in the sorbate hydrocarbon skeleton. Similarly to the reference stationary phases (Chromosorb W, Porapak P), electrostatic orientation interactions are also important in this case. In contrast to the reference phases, cyclic hydrocarbons are retarded substantially less than the corresponding linear homologues on *p*-*tert*-butylcalix[4]arene phase ($IRT_{n\text{-alkanes}}^{\text{b.p.}} = -10$ to -26.2) owing to a

certain specific non-dispersion interaction. In agreement with the reference phases, branched alkanes are retarded less than the linear isomers.

4.2. Retention behaviour of aromatic hydrocarbons

The measurements yielded linear dependences of the retention data on selected molecular descriptors for toluene, ethylbenzene, *n*-propylbenzene and *n*-butylbenzene on the *p*-*tert*-butylcalix[4]arene stationary phase (Table 1). A similar behaviour is also exhibited by *m*-xylene and *p*-ethyltoluene. On the basis of these results, stereochemical calculations and published work [1,2], a reference homologous series (RHS) was formulated including lower *n*-alkylbenzenes (toluene, ethylbenzene, *n*-propylbenzene and *n*-butylbenzene). This series meets the condition of a defined sorbate-stationary phase interaction mechanism that is the same in character for all the members of the series [the correlation coefficient is 0.999998 for the $-\Delta H = f(-\Delta S)$ dependence]. It can be assumed that the predominating interaction for RHS is guest inclusion into the *p*-*tert*-butylcalix[4]arene cavity, involving $\text{CH}_3(\text{host})-\pi(\text{guest})$ interactions and possibly also $\text{CH}_3(\text{guest})-\pi(\text{host})$ interactions. The increased retardation of benzene ($IRT_{\text{RHS}}^{\text{b.p.}} = +29.4$), as the "zero" RHS member, is probably also caused by a high probability of a suitable

Table 1
Linear dependences of the retention data obtained on *p*-*tert*-butylcalix[4]arene on selected molecular descriptors for toluene, ethylbenzene, *n*-propylbenzene and *n*-butylbenzene

Functional dependence	$y = A + Bx$		
	A	B	r
$\text{Log } k = f(\text{b.p.})$	-2.5055	0.0151	0.9999
$\text{Log } k = f(MV)$	-3.1890	0.0223	0.9994
$\text{Log } k = f(\alpha)$	-3.2715	0.0016	0.9999
$\Delta H = f(\text{b.p.})$	-1.7355	0.2756	0.9993
$\Delta S = f(\text{b.p.})$	9.1010	0.2428	0.9993
$\Delta G_{\text{m.o.c.}} = f(\text{b.p.})$	-4.7675	0.1947	0.9993

Column temperature, 60.0°C; nitrogen flow-rate, 7.5 ml min⁻¹; volume of sample, 70 μ l (vapour).

steric arrangement of the benzene molecule during its entry into the calixarene cavity. This specific interaction mechanism for benzene on a phase containing *p-tert.*-butylcalix[4]arene permits complete separation of benzene (b.p. = 80.1°C) from aliphatic and alicyclic hydrocarbons (hexane and cyclohexane, b.p. = 69–81°C) (Fig. 2).

Linear dependences of the retention data for RHS and xylenes on Chromosorb W and Porapak P (Fig. 3) on selected molecular descriptors and their comparison with the retention behaviour on *p-tert.*-butylcalix[4]arene demonstrate that *o*-xylene is retarded significantly less than RHS ($IRT_{RHS}^{b.p.} = -12.5$) and that *m*-xylene elutes in agreement with RHS ($IRT_{RHS}^{b.p.} = -3.9$), as can be seen in Fig. 4. *p*-Xylene is retarded significantly more strongly than the other isomers (Table 2).

The retention of ethyltoluenes was primarily evaluated with respect to the Porapak P reference phase. Whereas *p*-ethyltoluene is eluted in agreement with RHS on the *p-tert.*-butylcalix[4]arene phase ($IRT_{RHS}^{b.p.} = -1.6$), *m*- and *o*-ethyltoluene are retarded significantly less (the respective $IRT_{RHS}^{b.p.}$ values are -11.5 and -23.3 ; see Fig. 4).

A decreased retardation was found for isopropylbenzene ($IRT_{RHS}^{b.p.} = -12.9$), 1,3,5- and 1,2,4-trimethylbenzenes ($IRT_{RHS}^{b.p.} = -18.7$ and -22.2 , respectively), *tert.*-butylbenzene ($IRT_{RHS}^{b.p.} = -35.6$), *sec.*-butylbenzene ($IRT_{RHS}^{b.p.} = -25.7$) and *p*-cymene ($IRT_{RHS}^{b.p.} = -15.1$).

The experimental thermodynamic data relating to the sorbate–stationary phase interaction are given in Table 3. The magnitude of the enthalpy ΔH (the mean differential molar enthalpy) corresponds to weak bonding interactions. The relatively high magnitude of entropy ΔS (the mean differential molar entropy) suggests a significant contribution of the degree of ordering in the system to the overall interaction mechanism. A comparison of the thermodynamic data for cyclohexane and benzene (or RHS) demonstrates that the presence of an aromatic system in the guest causes an increase in ΔH of ca. 3.5 kJ mol⁻¹ and in ΔS of 3.0 J mol⁻¹ K⁻¹.

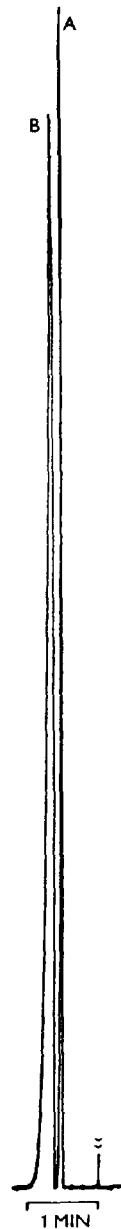


Fig. 2. Chromatogram of separation of benzene from hexane and cyclohexane. Micropacked column (1.64 m × 1 mm I.D.) containing *p-tert.*-butylcalix[4]arene, $T_c = 31.0^\circ\text{C}$. Peaks: A = hexane (b.p. = 69.0°C) and cyclohexane (b.p. = 80.7°C); B = benzene (b.p. = 80.1°C).

The reference homologous series for the thermodynamic measurements consisted of toluene, ethylbenzene and *p*-ethyltoluene [for

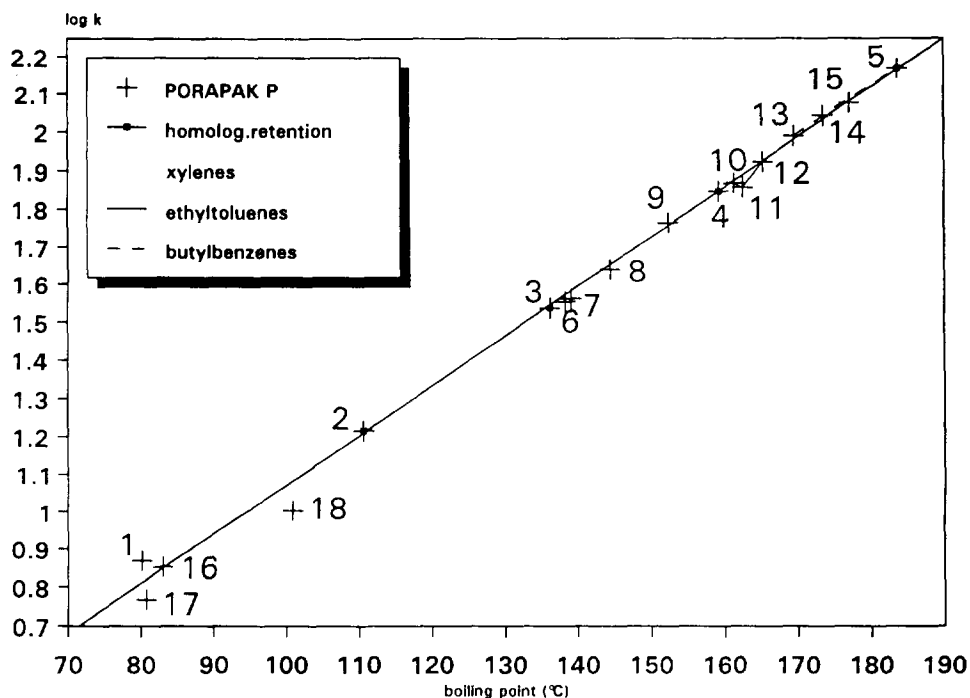


Fig. 3. Retention behaviour of aromatics on the Porapak P stationary phase: log (capacity factor) dependence on boiling point. Column temperature, 130.0°C; nitrogen flow-rate, 20.0 ml min⁻¹; volume of sample, 50 μ l (vapour). 1 = Benzene; 2 = toluene; 3 = ethylbenzene; 4 = *n*-propylbenzene; 5 = *n*-butylbenzene; 6 = *p*-xylene; 7 = *m*-xylene; 8 = *o*-xylene; 9 = isopropylbenzene; 10 = *m*-ethyltoluene; 11 = *p*-ethyltoluene; 12 = *o*-ethyltoluene; 13 = *tert.*-butylbenzene; 14 = *sec.*-butylbenzene; 15 = *p*-cymene; 16 = cyclohexene; 17 = cyclohexane; 18 = methylcyclohexane.

the dependence $\Delta H = A + B$ (b.p.) it was calculated that $A = -1.7355$, $B = 0.2756$, $r = 0.9993$. It can be seen from Fig. 5 that there is a significant increase in ΔH (in comparison with RHS) for *p*-xylene [$\Delta(\Delta H) = +1.4$ kJ mol⁻¹], which corresponds to an increased entropy [$\Delta(\Delta S) = +1.8$ J mol⁻¹ K⁻¹] and retardation in the column ($IRT_{RHS}^{b.p.} = +5.6$). This is probably caused by an increased probability of a suitable spatial orientation of the molecule during interaction with the *p-tert.*-butylcalix[4]arene cavity compared with, e.g., toluene. The significant enthalpy decreases for *o*-xylene [$\Delta(\Delta H) = -2.2$ kJ mol⁻¹], *m*-ethyltoluene [$\Delta(\Delta H) = -2.4$ kJ mol⁻¹] and *o*-ethyltoluene [$\Delta(\Delta H) = -4.8$ kJ mol⁻¹] correspond to the retention behaviour of these compounds, as discussed above. Differences have been found between the experimental

thermodynamic data and the retention behaviour for benzene and isopropylbenzene. The same holds for the entropy changes.

Whereas the thermodynamic data for ethyltoluene isomers are in agreement with their elution order, there is disagreement for xylene isomers.

It follows from the above findings that benzene, lower *n*-alkyl derivatives (toluene to *n*-butylbenzene), *p*-dialkylbenzenes (*p*-xylene, *p*-ethyltoluene) and *m*-xylene are probably included in the *p-tert.*-butylcalix[4]arene cavity. Steric hindrances to inclusion probably appear for *o*-dialkylbenzenes (*o*-xylene, *o*-ethyltoluene), *m*-ethyltoluene in the presence of at least one isopropyl or a more voluminous substituent on the benzene ring and for trisubstituted benzenes.

It should be pointed out that the selectivity of

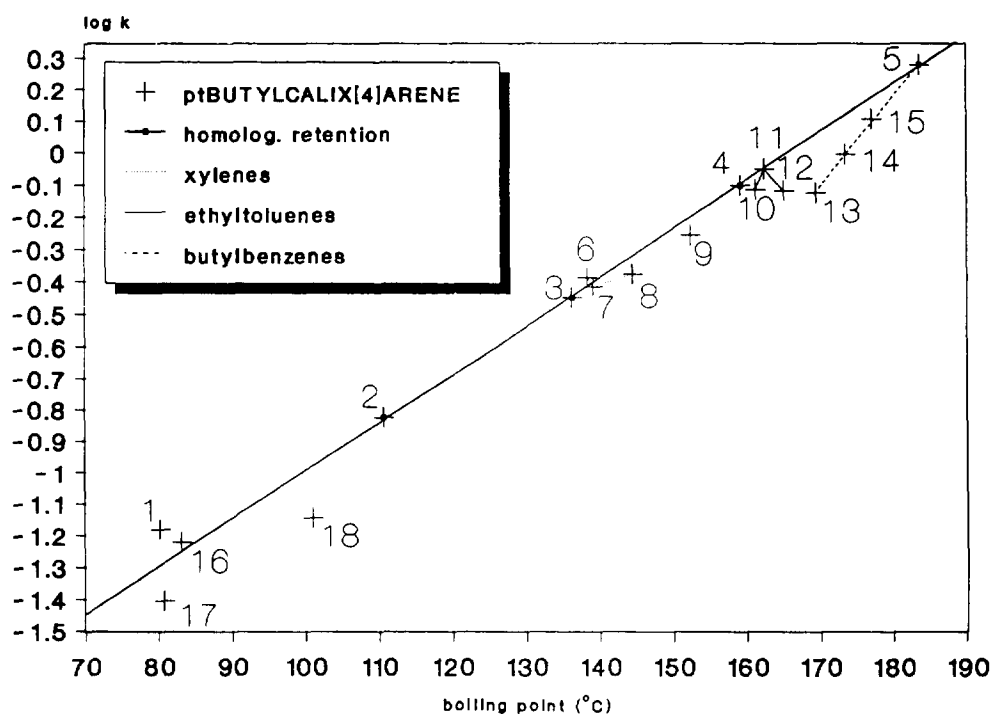


Fig. 4. Retention behaviour of aromatics: log (capacity factor) dependence on boiling point. Column temperature, 60.0°C; nitrogen flow-rate, 7.5 ml min⁻¹; volume of sample, 70 μl (vapour). 1 = Benzene; 2 = toluene; 3 = ethylbenzene; 4 = *n*-propylbenzene; 5 = *n*-butylbenzene; 6 = *p*-xylene; 7 = *m*-xylene; 8 = *o*-xylene; 9 = isopropylbenzene; 10 = *m*-ethyltoluene; 11 = *p*-ethyltoluene; 12 = *o*-ethyltoluene; 13 = *tert.*-butylbenzene; 14 = *sec.*-butylbenzene; 15 = *p*-cymene; 16 = cyclohexene; 17 = cyclohexane; 18 = methylcyclohexane.

Table 2

Linear dependences of the retention data for xylenes on some molecular descriptors

Column	Functional dependence	$y = A + Bx$			<i>IRT</i> _{xylenes} value for <i>p</i> -xylene
		<i>A</i>	<i>B</i>	<i>r</i>	
Chromosorb W	Log <i>k</i> = <i>f</i> (b.p.)	-1.7703	0.0084	0.9991	-1.0
	Log <i>k</i> = <i>f</i> (<i>MV</i>)	1.7763	-0.0194	1.0000	+0.6
	Log <i>k</i> = <i>f</i> (α)	8.9566	-0.6705	0.9989	-0.4
Porapak P	Log <i>k</i> = <i>f</i> (b.p.)	-0.4182	0.0142	0.9990	+2.0
	Log <i>k</i> = <i>f</i> (<i>MV</i>)	5.6015	-0.0329	0.9970	+2.2
	Log <i>k</i> = <i>f</i> (α)	17.7024	-1.1318	0.9914	+0.6
<i>p-tert.</i> -Butylcalix[4]arene	Log <i>k</i> = <i>f</i> (b.p.)	-1.4658	0.0075	-	+8.5
	Log <i>k</i> = <i>f</i> (<i>MV</i>)	1.7845	-0.0179	-	+8.9
	Log <i>k</i> = <i>f</i> (α)	1.8428	-0.6494	-	+9.2

On *p-tert.*-butylcalix[4]arene stationary phase, *IRT* value according to *m/o*-xylene retention level. Column temperature, 60.0°C (Chromosorb W and *p-tert.*-butylcalix[4]arene) and 130°C (Porapak P); nitrogen flow-rate, 7.5 ml min⁻¹; volume of sample, 70 μl (vapour).

Table 3

Experimental values of the thermodynamic properties of some aromatics on the *p*-*tert*-butylcalix[4]arene stationary phase

Sorbates	$-\Delta H \pm L_{1,2}$ (kJ mol ⁻¹)	$-\Delta S \pm L_{1,2}$ (J mol ⁻¹ K ⁻¹)	$-\Delta G \pm L_{1,2}$ (333.1 K) (kJ mol ⁻¹)
Cyclohexane	17.1 ± 0.3	25.2 ± 0.1	8.7 ± 0.4
Methylcyclohexane	22.9 ± 0.3	31.1 ± 0.3	12.5 ± 0.6
Cyclohexene	17.4 ± 0.3	24.8 ± 0.3	9.1 ± 0.6
Benzene	20.6 ± 0.2	28.2 ± 0.1	11.2 ± 0.3
Toluene	28.9 ± 0.2	36.1 ± 0.7	16.9 ± 0.9
Ethylbenzene	35.5 ± 0.2	41.9 ± 0.1	21.5 ± 0.3
<i>p</i> -Xylene	37.8 ± 0.3	44.5 ± 0.1	23.0 ± 0.4
<i>m</i> -Xylene	35.5 ± 0.2	41.8 ± 0.1	21.6 ± 0.3
<i>o</i> -Xylene	35.9 ± 0.2	41.8 ± 0.0	22.0 ± 0.2
Isopropylbenzene	39.6 ± 0.2	45.7 ± 0.1	24.4 ± 0.3
<i>m</i> -Ethyltoluene	40.3 ± 0.3	45.3 ± 0.1	25.2 ± 0.4
<i>p</i> -Ethyltoluene	43.2 ± 0.3	48.7 ± 0.1	27.0 ± 0.4
<i>o</i> -Ethyltoluene	39.0 ± 0.2	43.6 ± 0.1	24.5 ± 0.3

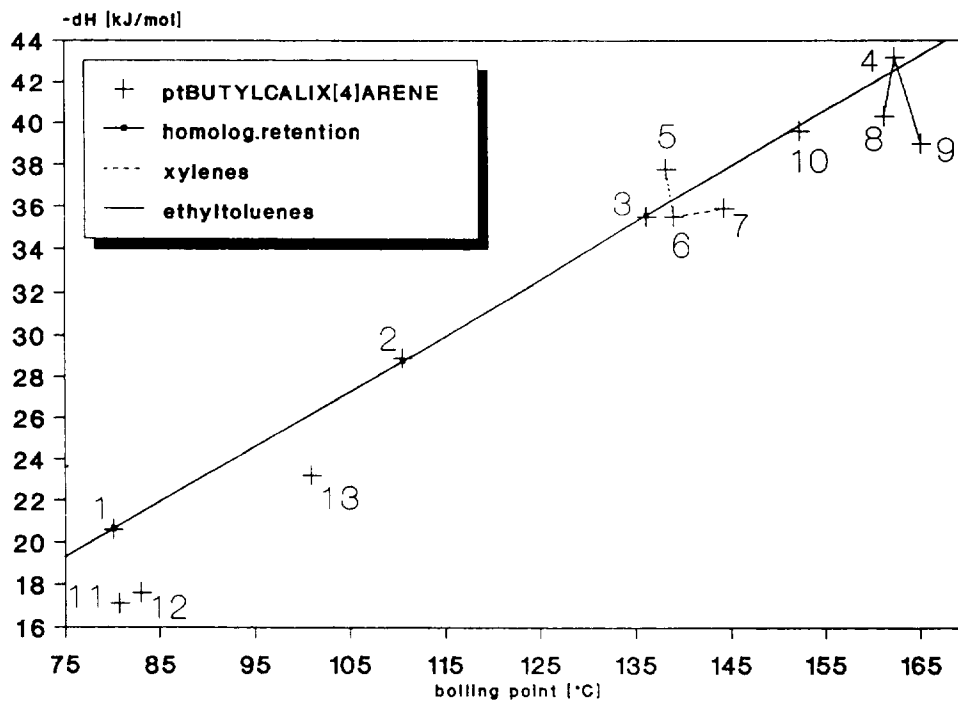
Column temperature range, 50.0–100.0°C; nitrogen flow-rate, 7.5 ml min⁻¹; volume of sample, 70 μl (vapour).

Fig. 5. Thermodynamic properties of aromatics: dependence of mean differential molar enthalpy (ΔH) on boiling point. Column temperature, 50.0–100.0°C; nitrogen flow-rate, 7.5 ml min⁻¹; volume of sample, 70 μl (vapour). 1 = Benzene; 2 = toluene; 3 = ethylbenzene; 4 = *p*-ethyltoluene; 5 = *p*-xylene; 6 = *m*-xylene; 7 = *o*-xylene; 8 = *m*-ethyltoluene; 9 = *o*-ethyltoluene; 10 = isopropylbenzene; 11 = cyclohexane; 12 = cyclohexene; 13 = methylcyclohexane.

p-tert.-butylcalix[4]arene towards *p*-xylene found here is in agreement with the published results for selective extraction [18].

4.3. Retention behaviour of halo derivatives

The dependences between the retention data and selected molecular descriptors for *n*-chloroalkanes (C₄–C₈) on both the Porapak P reference phase and the *p*-tert.-butylcalix[4]arene phase are linear (Table 4). The interaction mechanism involves dispersion and orientation dipole interactions.

The bromo, iodo and chloro derivatives elute together according to a single retention dependence on the Porapak P reference phase, but retardation increases in the order I < Br < Cl on the *p*-tert.-butylcalix[4]arene phase. Halocycloalkanes are retarded more than the linear isomers on Porapak P ($IRT_{C_4-C_8Cl}^{b,p} = +6.5$ to $+10.7$), but significantly less on *p*-tert.-butylcalix[4]arene ($IRT_{C_4-C_8Cl}^{b,p} = -41.7$ to -50.9). Dibromobutanes elute over a narrow time interval on Porapak P, in agreement with *n*-haloalkanes ($IRT_{C_4-C_8Cl}^{b,p} = -0.4$ to $+7.2$), whereas on *p*-tert.-butylcalix[4]arene they are retarded significantly less and over a wide time interval ($IRT_{C_4-C_8Cl}^{b,p} = -51.0$ to -5.7). The elution order is identical with the order of boiling points.

There exists a group of molecules, including iodomethane, diiodomethane, iodoethane and bromoethane, whose molar volumes do not exceed 95 cm³ mol⁻¹ and that are retarded, with respect to *n*-haloalkanes, significantly more on *p*-tert.-butylcalix[4]arene than on Porapak P. It is probable that inclusion of these molecules in the calixarene cavity contributes significantly to the overall interaction.

The experimental retention data for di-, tri- and tetrachloromethane on Chromosorb W exhibit roughly linear dependences of log *k* on selected molecular descriptors (b.p., *MV*, α , $1/\epsilon$, μ^2 , $\alpha + \mu^2$). The retardation of tetrachloromethane on Porapak P is decreased, probably owing to a decrease in electrostatic interaction between the sorbate and the aromatic system of Porapak P. A further decrease in tetrachloromethane retention compared with di- and trichloromethane was observed on *p*-tert.-butylcalix[4]arene. In view of data published earlier [5,11], it is probable that the molecules of di- and trichloromethane are included in the *p*-tert.-butylcalix[4]arene cavity. The decrease in the tetrachloromethane retardation is apparently caused by non-existence of CH- π interactions between the tetrachloromethane molecule and the calixarene aromatic system, which seems to be an important factor for inclusion of this sorbate in the *p*-tert.-butylcalix[4]arene cavity.

Table 4
Linear dependences of the retention data on some molecular descriptors for *n*-haloalkanes (1-chlorobutane to 1-chlorooctane) on selected stationary phases

Column	Functional dependence	$y = A + Bx$		
		A	B	r
Porapak P	Log <i>k</i> = f (b.p.)	-0.3973	0.0136	1.000
	Log <i>k</i> = f (<i>MV</i>)	-1.6318	0.0220	0.9999
	Log <i>k</i> = f (α)	-1.3145	0.1968	0.9999
<i>p</i> -tert.-Butylcalix[4]arene	Log <i>k</i> = f (b.p.)	-2.6274	0.0161	0.9994
	Log <i>k</i> = f (<i>MV</i>)	-4.0711	0.0260	0.9996
	Log <i>k</i> = f (α)	-3.6972	0.2325	0.9996

Column temperature, 60.0°C (*p*-tert.-butylcalix[4]arene) and 130.0°C (Porapak P); nitrogen flow-rate, 7.5 ml min⁻¹; volume of sample, 70 μ l (vapour).

4.4. Retention behaviour of alcohols

The dependences of the retention data on selected molecular descriptors for *n*-alkanols from methanol to *n*-octanol on the Porapak P reference phase are linear (Table 5) and dispersion interactions predominate. In contrast to Porapak P, where hydroxyl groups apparently do not participate in the interaction mechanism, on the *p*-*tert*-butylcalix[4]arene phase strong interactions of hydroxyl groups with phenolic hydroxyls are exhibited.

Methanol and ethanol deviate significantly from linear dependences between the retention data and selected molecular descriptors for *p*-*tert*-butylcalix[4]arene (Table 5): $IRT_{C_3-C_6OH}^{b.p.} = +98.6$ and $+41.5$, respectively, $IRT_{C_3-C_6OH}^{MV} = +254.2$ and $+49.2$, respectively, $IRT_{C_3-C_6OH}^{\alpha} = +229.9$ and $+50.8$, respectively (Fig. 6). It can be assumed that this pronounced retardation is caused by inclusion of the methanol and ethanol molecules in the *p*-*tert*-butylcalix[4]arene cavity.

In contrast to the Porapak P reference phase, branched alkanols are retarded significantly less than the isomeric *n*-alkanols on *p*-*tert*-butylcalix[4]arene ($IRT_{C_3-C_6OH}^{b.p.} = -27.4$ to -47.9), see Fig. 6, except for *tert*-butanol ($IRT_{C_3-C_6OH}^{b.p.} = +4.0$). Thus, *p*-*tert*-butylcalix[4]arene permits the complete separation of butanol isomers, compared with Chromosorb W (resolution *iso*-

n- = 1.4 compared with 0.6 and *tert*-/*iso*- = 1.5 compared with 0.9). In contrast to Porapak P, alcohols with a hydroxyl group inside the alkyl chain are retarded significantly less than the isomeric 1-alkanols ($IRT_{C_3-C_6OH}^{b.p.} = -26.6$ to -83.5), see Fig. 6.

4.5. Retention behaviour of ethers

On the reference phases, di-*n*-alkyl ethers (C_4-C_{12}) exhibit linear dependences of the retention data on b.p., *MV*, α and $\alpha + \mu^2$ (Table 6). Diisopropyl ether is retarded less on both phases ($IRT_{C_4-C_{12}O}^{b.p.} = -11.9$ on Chromosorb W, and -48.0 on Porapak P), tetrahydrofuran is retarded significantly more on Porapak P ($IRT_{C_4-C_{12}O}^{b.p.} = +30.8$). On *p*-*tert*-butylcalix[4]arene, di-*n*-alkyl ethers (C_4-C_{14}) yield linear dependences of the retention data on b.p., *MV*, α and $\alpha + \mu^2$ (Table 6). Cyclic ethers are eluted in agreement with *n*-alkyl ethers. Diisopropyl ether is retarded perceptibly less than the isomeric di-*n*-propyl ether ($IRT_{C_4-C_{14}O}^{b.p.} = -36.0$).

5. Conclusions

The results obtained indicate that the QSRR method for treatment of GSC retention data is

Table 5

Linear dependences of the retention data on some molecular descriptors for *n*-alkanols on selected stationary phases

Column	Functional dependence	$y = A + Bx$		
		A	B	r
Porapak P (methanol to <i>n</i> -octanol)	$\text{Log } k = f(\text{b.p.})$	-1.3240	0.0181	0.9998
	$\text{Log } k = f(MV)$	-1.0603	0.0206	0.9993
	$\text{Log } k = f(\alpha)$	-0.8232	0.1869	0.9995
	$\text{Log } k = f(\mu)$	42.1156	24.8532	0.9897
	$\text{Log } k = f(\alpha + \mu^2)$	-1.3338	0.1844	0.9965
<i>p</i> - <i>tert</i> -Butylcalix[4]arene (<i>n</i> -propanol to <i>n</i> -hexanol)	$\text{Log } k = f(\text{b.p.})$	-3.0838	0.0291	0.9984
	$\text{Log } k = f(MV)$	-2.8509	0.0374	0.9985
	$\text{Log } k = f(\alpha)$	-2.4428	0.3150	0.9985
<i>p</i> - <i>tert</i> -Butylcalix[4]arene (methanol to <i>n</i> -butanol)	$\text{Log } k = f(\mu)$	53.1336	31.8010	0.9984

Column temperature, 60.0°C (*p*-*tert*-butylcalix[4]arene) and 130.0°C (Porapak P); nitrogen flow-rate, 7.5 ml min⁻¹; volume of sample, 70 μ l (vapour).

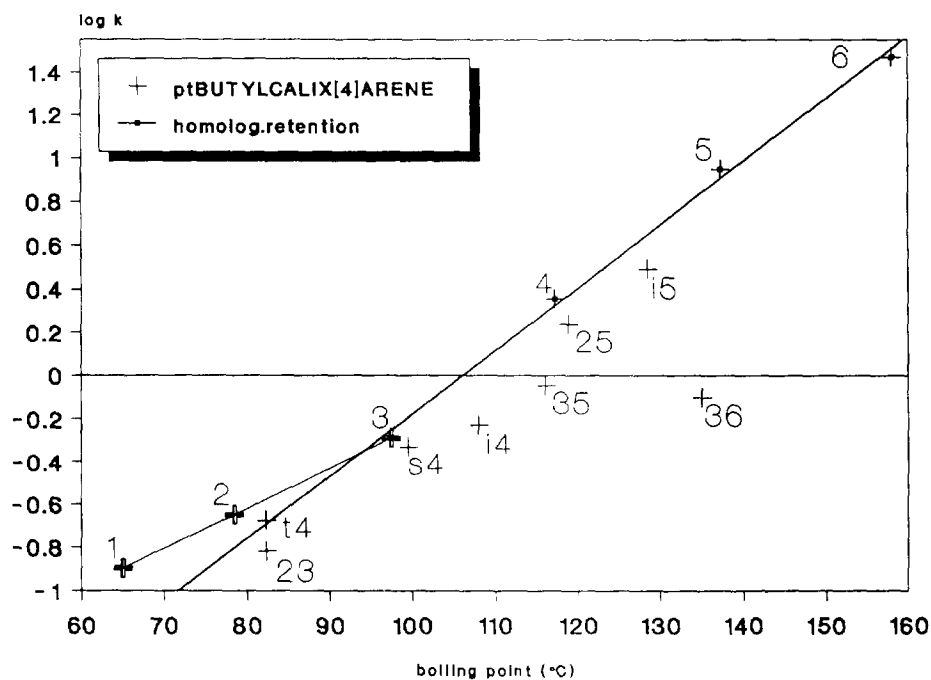


Fig. 6. Retention behaviour of alcohols: dependence of log (capacity factor) on boiling point. Column temperature, 60.0°C; nitrogen flow-rate, 7.5 ml min⁻¹; volume of sample, 70 μl (vapour). 1 = Methanol; 2 = ethanol; 3 = 1-propanol; 4 = 1-butanol; 5 = 1-pentanol; 6 = 1-hexanol; i4 = *tert.*-butanol; s4 = *sec.*-butanol; i4 = isobutanol; i5 = isopentanol; 23 = 2-propanol; 25 = 2-pentanol; 35 = 3-pentanol; 36 = 3-hexanol.

Table 6

Linear dependences of the retention data on some molecular descriptors for *n*-alkyl ethers (diethyl ether to di-*n*-heptyl ether) on selected stationary phases

Column	Functional dependence	$y = A + Bx$		
		A	B	r
Chromosorb W	$\text{Log } k = f(\text{b.p.})$	-2.1605	0.0137	0.9978
	$\text{Log } k = f(MV)$	-3.9829	0.0221	0.9980
	$\text{Log } k = f(\alpha)$	-3.4455	0.1973	0.9974
	$\text{Log } k = f(\alpha + \mu^2)$	-3.7026	0.1962	0.9985
Porapak P	$\text{Log } k = f(\text{b.p.})$	0.3660	0.0130	0.9998
	$\text{Log } k = f(MV)$	-2.1310	0.0213	0.9996
	$\text{Log } k = f(\alpha)$	-1.6152	0.1903	0.9998
	$\text{Log } k = f(\alpha + \mu^2)$	1.8586	0.1888	0.9992
<i>p-tert.</i> -Butylcalix[4]arene	$\text{Log } k = f(\text{b.p.})$	-2.1670	0.0146	0.9993
	$\text{Log } k = f(MV)$	182.8840	50.8050	0.9988
	$\text{Log } k = f(\alpha)$	24.5802	8.9153	1.0000
	$\text{Log } k = f(\alpha + \mu^2)$	2.1039	9.6772	0.9993

Column temperature, 60.0°C (Chromosorb W and *p-tert.*-butylcalix[4]arene) and 130.0°C (Porapak P); nitrogen flow-rate, 7.5 ml min⁻¹; volume of sample, 70 μl (vapour).

suitable for studying the selective properties of *p*-*tert*-butylcalix[4]arene under gas chromatographic conditions. The newly introduced quantity IRT_v^D permits the quantitative evaluation of deviations in the retention behaviour within homologous series. It is probable that *p*-*tert*-butylcalix[4]arene forms, under GSC conditions, inclusion complexes with benzene, its lower *n*-alkyl derivatives (toluene to *n*-butylbenzene), *p*-dialkylbenzenes (*p*-xylene, *p*-ethyltoluene), *m*-xylene, dichloromethane, trichloromethane, methanol and ethanol. Steric hindrance to inclusion in the *p*-*tert*-butylcalix[4]arene cavity presumably arises with *o*-dialkylbenzenes (*o*-xylene, *o*-ethyltoluene), *m*-ethyltoluene in the presence of at least one isopropyl or a more bulky substituent on the benzene ring and trisubstituted benzenes. It is probable that the presence of CH– π interactions is decisive for the formation of *p*-*tert*-butylcalix[4]arene inclusion complexes with the studied neutral organic molecules under GSC conditions, as follows from the example of tetrachloromethane. In addition, phenolic hydroxyls located at the narrower edge of the calixarene molecule participate strongly in the overall interaction mechanism. A more detailed mechanism of the sorbate–calixarene interactions is still unknown. Our statements about probable inclusion complexes should be complemented by further more exact methods (NMR spectroscopy, X-ray crystallography); work on these problems is in progress.

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References

- [1] M. Coruzzi, G.D. Andreetti, V. Bocchi, A. Pochini and R. Ungaro, *J. Chem. Soc., Perkin Trans. 2*, (1982) 1133.
- [2] G.D. Andreetti, R. Ungaro and A. Pochini, *J. Chem. Soc., Chem. Commun.*, (1979) 1005.
- [3] G.D. Andreetti, in J. Vicens and V. Böhmer (Editors), *Calixarenes, a Versatile Class of Macrocyclic Compounds*, Kluwer, Dordrecht, 1991, p. 111.
- [4] R. Ungaro, A. Pochini, G.D. Andreetti and P. Domiano, *J. Chem. Soc., Perkin Trans. 2*, (1985) 197.
- [5] C.D. Gutsche, B. Dhawan, K.H. No and R. Muthukrishnan, *J. Am. Chem. Soc.*, 103 (1981) 3782.
- [6] M.A. McKervey, E.M. Seward, G. Ferguson and B.L. Ruhl, *J. Org. Chem.*, 51 (1986) 3581.
- [7] G.D. Andreetti, O. Ori, F. Ugozzoli, C. Alfieri, A. Pochini and R. Ungaro, *J. Inclusion Phenom.*, 6 (1988) 523.
- [8] K.-E. Bugge, W. Verboom, D.N. Reinhoudt and S. Harkema, *Acta Crystallogr., Sect. C*, 48 (1992) 1848.
- [9] K. Suzuki, A.E. Armah, S. Fujii, K. Tomita, Z. Asfari and J. Vicens, *Chem. Lett.*, 10 (1991) 1699.
- [10] M. Perrin and S. Lecocq, *J. Crystallogr. Spectrosc. Res.*, 22 (1992) 619.
- [11] J.L. Atwood, S.G. Bott, C. Jones and C.L. Raston, *J. Chem. Soc., Chem. Commun.*, (1992) 1349.
- [12] T.-M. Liang, K.K. Laali, M. Cordero and C. Wesdemiotis, *J. Chem. Res. (S)*, (1991) 354.
- [13] E. Smolková-Keulemansová and L. Feltl, presented at the 2nd International Symposium on Clathrate Compounds and Molecular Inclusion Phenomena, Parma, Italy, 1982, abstracts, p. 45.
- [14] A. Mangia, A. Pochini, R. Ungaro and G.D. Andreetti, *Anal. Lett.*, 16 (1983) 1027.
- [15] R. Kaliszán, *Quantitative Structure–Chromatographic Retention Relationships*, Wiley, New York, 1987.
- [16] J.R. Conder and C.L. Young, *Physicochemical Measurements by Gas Chromatography*, Wiley, New York, 1986.
- [17] E.L. Arancibia, C.R. de Schaefer and M. Katz, *Chromatografia*, 33 (1992) 41.
- [18] J. Vicens, A.E. Armah, S. Fujii and K.-I. Tomita, *J. Inclusion Phenom.*, 10 (1991) 159.