

Thermal behaviour of some ester derivatives of *p*-*tert*-butyl calix[*n*]arene

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Abstract The thermal behaviour of three ester derivatives of *p*-*tert*-butyl calix[*n*]arene (*n* = 4, 6 and 8) in comparison with the parent calixarene was investigated by means of the thermogravimetric (TG) and differential thermogravimetric (DTG) analysis and differential scanning calorimetry (DSC). The thermal stability domains, the composition of the pyrolysis products and the thermal effects, were determined on the basis of TG, DTG and DSC plots registered in nitrogen flow. Attempts to analyse the evolved gases by TG-FTIR coupling were also performed. It was demonstrated that the stability of the calix[*n*]arene derivatives depends on both the size of the hydrophobic cavity and number of the substituting groups grafted on the calix[*n*]arene skeleton.

Keywords *p*-*tert*-butyl calix[*n*]arene · Calix[*n*]arene ester derivatives · Thermal analysis · Evolved gas analysis

Introduction

Calixarenes are cyclic oligomers originating from the base-catalysed condensation of *p*-substituted phenol with formaldehyde [1, 2]. Their characteristic architecture, i.e. phenolic units linked by methylene bridges to form a hydrophobic cavity, as well as the grafted functional groups, makes them capable of host–guest interaction with metallic

ions and neutral molecules [3–5]. Calix[*n*]arene derivatives can be synthesized by modification at the phenol OH groups (‘narrow rim’), e.g. esterification, etherification and in the *para*-position of the phenyl rings (‘wide rim’), e.g. sulphonation, nitration and alkylation [6–9]. Introduction of the functional groups in calixarenes skeleton allows the selectivity of the host–guest interaction to be controlled.

Calixarene derivatives incorporating ionophoric functional groups such as amine, amide or ester, grafted at the ‘narrow rim’, exhibit excellent extraction/complexation properties. The high ability of these calixarenes to form coordination compounds offers large utilization possibilities in the manufacture of sensitive membrane for electrical and optical sensors, elaboration of extraction methods for various cations, realization of modern recovery procedure and for the environmental protection [10–12]. In order to find new and efficient extracting reagents, new calix[*n*]arene derivatives functionalized at the ‘narrow rim’ with ethyl acetate, i.e. ester derivatives, were synthesized, investigated and reported in our previously studies [13].

Thermal analysis can offer useful information about the calix[*n*]arenes’ stability or the temperature range in which they can be used, without changing their composition and properties. According to the literature, the thermal analysis was used to investigate *p*-*tert*-butyl calix[4, 6, 8]arenes and their azoderivatives [14–19]. To the best of our knowledge, no similar information about the calixarene ester derivatives was reported yet.

In this study, we report about the thermal behaviour of some calix[*n*]arenes ester derivatives that were synthesized for the metal sequestration. For this purpose, thermal analysis and evolved gas analysis (EGA) by FTIR spectroscopy were used to investigate the totally substituted ester derivatives of *p*-*tert*-butyl calix[4, 6, 8]arene, in comparison with their parent calix[*n*]arenes.

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Experimental

Synthesis of the starting *p*-*tert*-butyl calix[*n*]arene ($n = 4, 6, 8$) and their ester derivatives

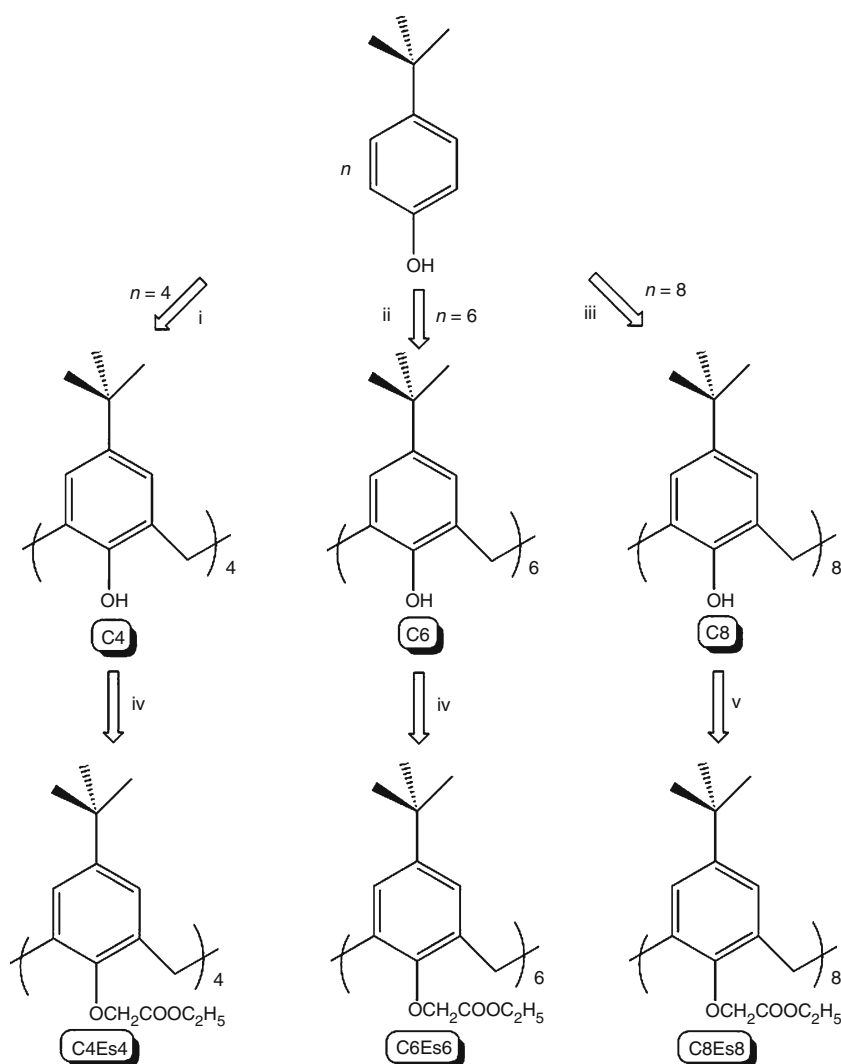
The starting *p*-*tert*-butyl calix[*n*]arenes (hereinafter **C4**, **C6** and **C8**) were synthesized by slightly modifying the procedure already described in the literature [20–22]. Ester derivatives of calix[*n*]arene (hereinafter **C4Es4**, **C6Es6** and **C8Es8**) were prepared by original procedures, by treating the parent calix[*n*]arene with ethyl bromoacetate in the presence of base (K_2CO_3 or NaH) and organic solvent (THF/DMF or acetone) [13]. All the compounds were purified by re-crystallization from toluene, chloroform or chloroform–ethanol mixture, followed by drying for 6 h,

under vacuum, at about 60 °C. The synthesis of *p*-*tert*-butyl calix[*n*]arene derivatives is illustrated in Fig. 1.

Investigation methods

Thermogravimetric (TG) analysis was performed using a Mettler Toledo TGA/SDTA851° Thermal Analysis System. The measurements were carried out in the temperature range of 25–1,000 °C, in alumina crucible, in nitrogen with a flow rate of 35 mL min⁻¹. The heating rate was 10 °C min⁻¹ and the sample weight was 13–25 mg. EGA was performed using a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with TG module, operating at 280 °C temperature. The composition of the evolved gases was performed using the instrument FTIR spectra library,

Fig. 1 Synthesis scheme of *p*-*tert*-butyl calix[*n*]arene derivatives



- i: Synthesis: CH_2O , NaOH, diphenylether; Recrystallization: $C_6H_5-CH_3$;
 ii: Synthesis: CH_2O , KOH, xylene; Recrystallization: CH_2Cl/CH_3CH_2OH ;
 iii: Synthesis: CH_2O , NaOH, xylene; Recrystallization: CH_2Cl ;
 iv: Synthesis: $BrCH_2COOC_2H_5$, K_2CO_3 , acetone; Recrystallization: CH_2Cl/CH_3CH_2OH ;
 v: Synthesis: $BrCH_2COOC_2H_5$, NaH, THF/DMF; Recrystallization: CH_2Cl/CH_3CH_2OH ;

i.e. HR Nicolet TG Vapour phase. Differential scanning calorimetry (DSC) was performed using a Mettler Toledo DSC 823^o/700 °C. The measurements were carried out in the 25–600 °C temperature range, in aluminium crucibles, under nitrogen flow (20 mL min⁻¹). The heating rate was 10 °C min⁻¹ and the sample weight was in the range of 2–7 mg.

Results and discussion

Three parent calix[*n*]arenes and three ester derivatives were prepared according to the scheme depicted in Fig. 1. The calixarene compounds were investigated by thermal analysis and EGA (Table 1). The starting point and the temperature domains of the decomposition stages as well as the partial and total weight loss (on TG plots), the weight loss maxima (on DTG plots), the temperature onset and maxima (on DSC plots) are determined for the parent calixarenes **C4**, **C6** and **C8** and for the corresponding ester derivatives **C4Es4**, **C6Es6** and **C8Es8**. The composition of the gases released during the decomposition process is also given.

The weight loss varies between 82.5 and 87.4 % for the parent calix[*n*]arenes, and between 77.1 and 77.6 % for the ester derivatives. The total esterification of calixarenes leads to the increase of the amount of the decomposition residue (black carbon) in agreement with their composition.

All the investigated compounds have two major decomposition stages associated with the weight loss step of 36–47 % that produces up to 430 °C and the weight loss step of 23–36 % that occurs up to 600 °C. The first major decomposition stage can be correlated with the ‘detachment’ of the *tert*-butyl groups for the parent calix[*n*]arenes and the removal of both ester and *tert*-butyl groups, for the ester derivatives. The second major decomposition step can be associated with the destruction of the hydrophobic cavity. Above 600 °C, a small weight loss step of 3–4 % can be noticed, in correlation with the partial burning of the residue, due to low content of oxygen in the samples.

In addition, two or one small weight loss steps could be noticed under 300 °C for the parent calixarene **C4** and correspondingly, **C6**. This could be associated with the removal of the solvent trapped in their small internal cavity. In fact, according to the literature data, the internal diameter of the cavity of the calixarenes under discussion is 3.0, 7.6 and 11.7 Å for compounds **C4**, **C6** and **C8**, respectively [23].

The thermal degradation of the parent calix[*n*]arenes starts at about 340–360 °C, in agreement with the literature data [15, 24]. For the ester derivatives, the thermal degradation starts at about 280–300 °C, thus illustrating that the esterification decreases the thermal stability of the calixarenes.

The heat flows associated with the phase change and the thermal decomposition of the calix[*n*]arene compounds were put in evidence on the DSC plots. The onset temperature and the peak temperature of the main peaks are summarised in Table 1. The good complementarity of the DSC and DTG peaks allows assigning the endothermic effects to the corresponding mass loss steps for solvent removal and gas evolving during the thermal decomposition. The exothermic DSC peaks (marked with b) observed for the ester derivatives were associated with their oxidative degradation promoted by the relative large amount of oxygen from the functional groups. The endothermic DSC peaks (marked a) associated with no weight-loss events, were assigned to the calixarene melting. In the case of **C6Es6** compound, an additional endothermic DSC peak (marked c) was noticed at 201 °C. This heat flow peak corresponds also to an event without mass loss that could be assigned to an intra- crystalline arrangement.

Mention has to be made that, while the DSC peaks associated with the phase changes are well defined, those related to the thermal dissociation are rather diffused, being formed from overlapping peaks. The sharp DSC peaks associated with the fusion heat always precede the large DSC peaks corresponding to calix[*n*]arenes thermal decomposition. In some cases, these peaks are partially overlapping, i.e. **C6** and **C8**. The melting temperature of the parent calix[*n*]arenes (expressed by T_{onset}) increases with the number of the aromatic rings as follows 341 °C (**C4**), 369 °C (**C6**) and 374 °C (**C8**). The rather low melting temperature for **C8** suggests that our product contains other cyclic oligomers that were incompletely removed during the re-crystallization stage [22]. The ester derivatives melt at relatively lower temperature than the parent calixarenes as follows 129 °C (**C4Es4**), 268 °C (**C6Es6**) and 230 °C (**C8Es8**). The relatively lower fusion temperature for **C8Es8** is probably in correlation with its impurity level.

The EGA allows assessing the processes that occur during the thermal treatment of the calix[*n*]arene derivatives. Figure 2 shows the DTG plots and Gram–Schmidt diagrams for the parent *p-tert*-butyl calix[*n*]arenes and their ester derivatives. The Gram–Schmidt diagrams, i.e. the FT-IR absorbance of the evolved gases in function of time as well as the DTG curves confirm that the thermal decomposition of the investigated calixarenes proceeds in two major stages, excepting *p-tert*-butyl calix[6]arene (**C6**) and *p-tert*-butyl calix[4]arene (**C4**), which, as already mentioned, exhibit additional peaks probably in relation with the solvent capture.

Figure 3 is dedicated to the 3D plots for FTIR absorbance of the evolved gases, in dependence on the TG time for the calixarene compounds with six interconnected aromatic rings.

Table 1 Thermal behaviour of parent calix[n]arene and *p-tert*-butyl calix[n]arene derivatives evaluated by TG, DSC and EGA

Sample code	TG data		DSC data			EGA results		
	Temperature domain/ °C	$T_{\text{onset}}/$ °C	$T_{\text{max}}/$ °C	$\Delta m/$ %	$\Delta m_T/$ %	$T_{\text{onset}}/$ °C	$T_{\text{max}}/$ °C	Composition of the evolved gas
C4	25–200	117	137	7.3	87.4	134	141	C ₆ H ₅ –CH ₃ , H ₂ O
	200–320	266	283	6.9	–	287	289	C ₆ H ₅ –CH ₃ , H ₂ O, CO ₂
	320–430	341	389	46.0	–	341 ^a ; 357	342 ^a ; 398	H ₂ O, CO ₂ , (CH ₃) ₃ CCH ₂ CH(CH ₃) ₂ , (CH ₃) ₃ CC ₆ H ₄ OH, C ₆ H ₅ –OH
	430–600	426	491	23.2	–	539	553	H ₂ O, CO ₂ , (CH ₃) ₃ CCH ₂ CH(CH ₃) ₂ , (CH ₃) ₃ CC ₆ H ₄ OH, C ₆ H ₅ –OH, CH ₄
	600–1,000	617	847	4.0	–	–	–	H ₂ O, CO ₂ , CO, (CH ₃) ₃ CC ₆ H ₄ OH, C ₆ H ₅ –OH
C4Es4	25–430	305	351	46.2	77.1	129 ^a , 292 ^b	132 ^a ; 344 ^b	H ₂ O, CO ₂ , CO, (CH ₃) ₃ CCH ₂ CH(CH ₃) ₂ , CH ₃ COOC ₂ H ₅ , CH ₃ CH ₂ OH
	430–600	442	485	27.2	–	449	516	H ₂ O, CO ₂ , CO, (CH ₃) ₃ CCH ₂ CH(CH ₃) ₂ , (CH ₃) ₃ CC ₆ H ₄ OH, CH ₄
	600–1,000	662	858	3.7	–	–	–	H ₂ O, CO ₂ , CO, CH ₄ , (CH ₃) ₃ CC ₆ H ₄ OH, C ₆ H ₅ –OH
C6	25–280	210	231	10.8	85.6	219	239	CHCl ₃
	280–430	362	388	35.6	–	369 ^a ; 380	373 ^a ; 388	H ₂ O, CO ₂ , (CH ₃) ₃ CCH ₂ CH(CH ₃) ₂ , (CH ₃) ₃ CC ₆ H ₄ OH, C ₆ H ₅ –OH
	430–600	452	484	35.6	–	472	485	H ₂ O, CO ₂ , (CH ₃) ₃ CCH ₂ CH(CH ₃) ₂ , (CH ₃) ₃ CC ₆ H ₄ OH, CH ₄
	600–1,000	615	825	3.6	–	–	–	H ₂ O, CO ₂ , CO, (CH ₃) ₃ CCH ₂ CH(CH ₃) ₂
C6Es6	25–430	284	345	42.5	77.6	198 ^c ; 268 ^a , 273 ^b	201 ^c ; 270 ^a , 327 ^b	H ₂ O, CO ₂ , (CH ₃) ₃ CCH ₂ CH(CH ₃) ₂ , CH ₃ COOC ₂ H ₅ , CH ₃ CH ₂ OH
	430–600	444	488	30.6	–	435	515	H ₂ O, CO ₂ , CO, C ₆ H ₅ –OH, (CH ₃) ₃ CCH ₂ CH(CH ₃) ₂ , (CH ₃) ₃ CC ₆ H ₄ OH, CH ₄
C8	600–1,000	606	843	4.5	–	–	–	H ₂ O, CO ₂ , CO, C ₆ H ₅ –OH
	25–430	360	387	47.0	82.5	374 ^a ; 389	382 ^a ; 394	H ₂ O, CO ₂ , (CH ₃) ₃ CCH ₂ CH(CH ₃) ₂ , (CH ₃) ₃ CC ₆ H ₄ OH, C ₆ H ₅ –OH
	430–600	435	481	31.7	–	482	485	H ₂ O, CO ₂ , (CH ₃) ₃ CCH ₂ CH(CH ₃) ₂ , (CH ₃) ₃ CC ₆ H ₄ OH, C ₆ H ₅ –OH, CH ₄
	600–1,000	611	823	3.8	–	–	–	H ₂ O, CO ₂ , CO, (CH ₃) ₃ CCH ₂ CH(CH ₃) ₂ , (CH ₃) ₃ CC ₆ H ₄ OH
C8Es8	25–430	290	347	42.1	77.2	230 ^a ; 283 ^b	232 ^a ; 329 ^b	H ₂ O, CO ₂ , (CH ₃) ₃ CCH ₂ CH(CH ₃) ₂ , CH ₃ COOC ₂ H ₅ , CH ₃ CH ₂ OH
	430–600	438	486	30.8	–	439	517	H ₂ O, CO ₂ , CO, (CH ₃) ₃ CCH ₂ CH(CH ₃) ₂ , C ₆ H ₅ –OH, (CH ₃) ₃ CC ₆ H ₄ OH, CH ₄
600–1,000	607	829	4.3	–	–	–	H ₂ O, CO ₂ , CO, C ₆ H ₅ –OH, CH ₄	

 T_{onset} starting temperature of the weight loss or the thermal effect, Δm weight loss for each stage, Δm_T total weight loss^a Melting process^b Exothermic process^c Crystalline arrangement process

Fig. 2 DTG plots and Gram–Schmidt diagrams for the calix[*n*]arene compounds

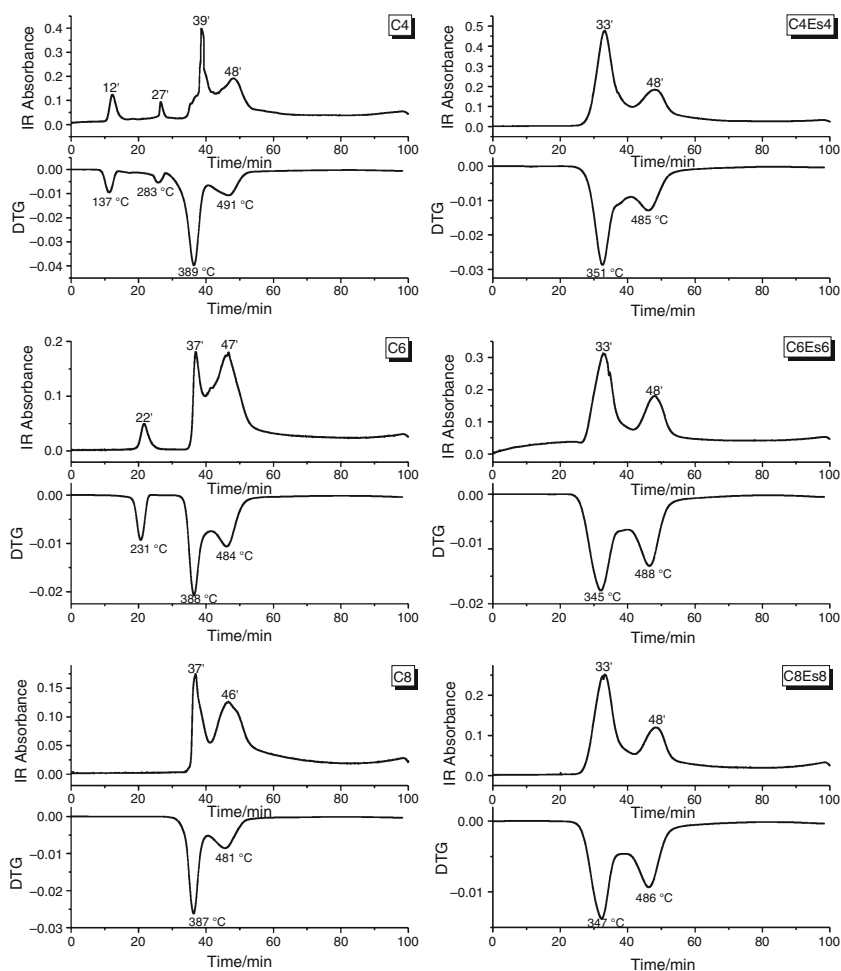
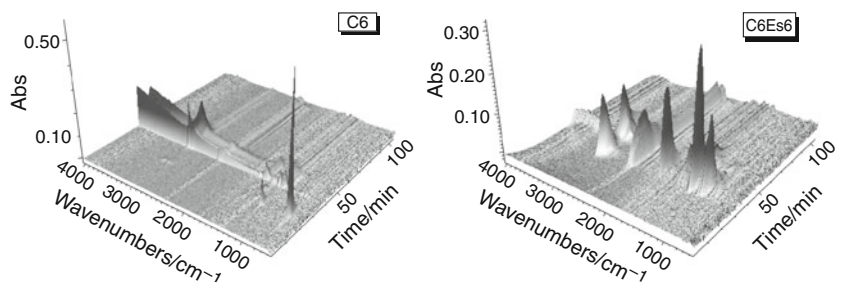


Fig. 3 3D images for the variation in time of the FTIR absorbance of gases released from the decomposition of the parent calix[6]arene (**C6**) and hexaester calix[6]arene derivative (**C6Es6**)

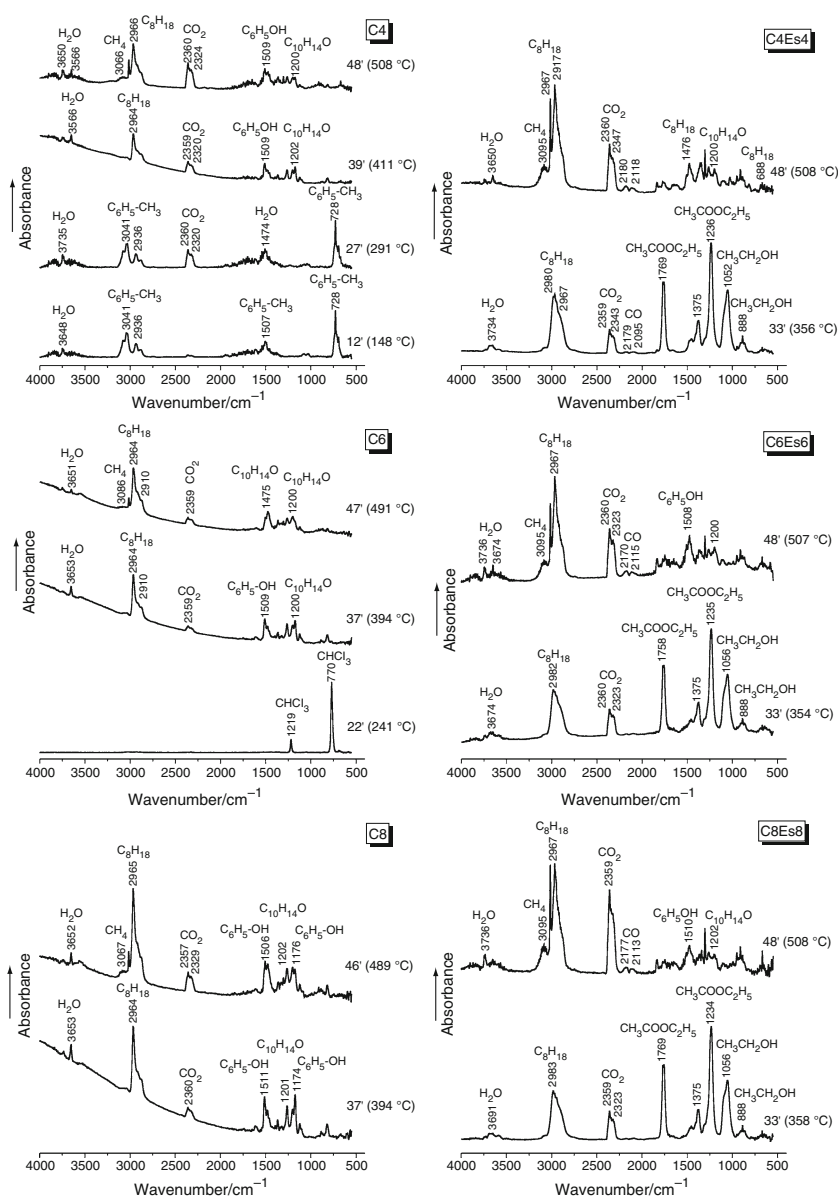


FTIR spectra of the gases evolved from the thermal decomposition of **C6** and **C6Es6** are dominated by the peak at $\sim 770\text{ cm}^{-1}$ (assigned to chloroform) and at $\sim 1,235\text{ cm}^{-1}$ (assigned to ethyl acetate), respectively. The FTIR spectra of ester derivatives are far more complicated than that of the corresponding parent calixarenes, thus illustrating the complexity of the thermal dissociation process. Similar results were obtained for the calixarene compounds with four and, correspondingly, eight aromatic rings.

The FT-IR profiles of gases evolved at different TG times, corresponding to maxima on the Gram–Schmidt diagrams, are depicted in Fig. 4.

The gases evolved from the decomposition of *p-tert*-butyl calix[4]arene are dominated by toluene in the first two stages (minute 12 and 27) and by 2,2,4-trimethylpentane (C_8H_{18}) in the last two stages (minute 39 and 48). The removal of the captured solvent in two stages could be explained by the fact that toluene is fixed extra-molecular (released at $148\text{ }^\circ\text{C}$) and intra-molecular (released at $291\text{ }^\circ\text{C}$). The compound trimethylpentane is generated from two *tert*-butyl radicals detached from **C4** and it is removed in two major steps. Phenol, *p-tert*-butyl-phenol ($\text{C}_{10}\text{H}_{14}\text{O}$ gas), methane, carbon dioxide and water were also identified in the release gases.

Fig. 4 FT-IR spectra of the gas evolved from the decomposition of the calixarenes compounds, at different TG moments



For *p*-*tert*-butyl calix[6]arene (**C6**), the gases evolved in the first stage (minute 22) are dominated by chloroform (captured from the re-crystallization medium). The gases from the two other major decomposition steps (minutes 37 and 47) are also dominated by 2,2,4-trimethylpentane (C_8H_{18}).

The gases generated from *p*-*tert*-butyl calix[8]arene contain mostly 2,2,4-trimethylpentane that is released in two major steps (minute 37 and 48). In this case, no solvent was detected by EGA.

The composition of the gases evolved during the decomposition stages, together with the corresponding weight loss, are presented in Table 1. It was revealed that the basic calixarenes **C4** and **C6** form inclusion compounds with toluene and chloroform, respectively. On the basis of TG plots and EGA results, the amount of the solvent

captured by the calixarene compounds could be calculated. In our synthesis conditions, one mol of *p*-*tert*-butyl calix[4]arene contains 1.17 mol toluene from which only 48.6 % is intra-molecular bounded, whereas one mol of *p*-*tert*-butyl calix[6]arene contains 0.99 mol chloroform, probably in an extra-molecular physical bonding. Results are in agreement with the literature data that indicate a host–guest ratio of about 1:1 [25–28].

In comparison with the parent calix[*n*]arenes, the ester calixarene derivatives generate, in addition, ethyl acetate and ethanol arising from the ester groups grafted at calixarene skeleton. The presence of 2,2,4-trimethylpentane, *p*-*tert*-butyl-phenol, phenol, carbon dioxide, carbon monoxide, methane and water was evidenced by EGA in almost all the thermal decomposition stages.

Conclusions

The thermal behaviour of the totally substituted ester derivatives of *p*-*tert*-butyl calix[4, 6, 8]arene, in comparison with their parent calix[*n*]arenes was evaluated on the basis of TG and DSC plots, in association with FTIR absorbance profiles of the gas evolved during the thermal analysis.

The calixarene ester derivatives have a total weight loss of 77.1–77.6 % (in comparison with 82.5–87.4 % for the parent calix[*n*]arenes), thus illustrating that the esterification leads to the increase of the amount of the decomposition residue (black carbon).

The thermal degradation of the calixarene ester derivatives starts at about 280–300 °C (in comparison with 340–360 °C for the parent calix[*n*]arenes); the grafting of the ester groups decreases the thermal stability of the calixarenes. The ester derivatives melt at relative smaller temperature than the starting calixarenes.

The thermal decomposition of all the investigated calixarene compounds takes place in two main stages, in the temperature range 320–600 °C, and it is accompanied by a major release of 2,2,4-trimethylpentane in association with carbon dioxide, *p*-*tert*-butyl-phenol, water and methane. The ester derivatives generate, in addition, ethyl acetate and ethanol. The parent calixarenes with relative small internal cavity capture solvent from the re-crystallization medium. In our synthesis conditions, one mol of *p*-*tert*-butyl calix[4]arene captures more than 1 mol toluene, equally trapped in extra- and intra-molecular position, whereas one mol of *p*-*tert*-butyl calix[6]arene fixes about 1 mol chloroform.

The thermal stability of the ester derivative of *p*-*tert*-butyl calix[4, 6, 8]arene is determined by the number of both the interconnected aromatic rings and the substituting ester groups grafted on the calix[*n*]arene skeleton. The thermal behaviour data complete the characteristics tableau of the calixarene-based compounds synthesized for the metal sequestration.

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