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Thermal analysis of two series *mono*- and *di*-azocalix[4]arene derivatives

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Abstract In the present study, thermal decomposition of *mono*- and *di*-azocalix[4]arene derivatives (**A1**–**A8** and **B1**–**B8**) was investigated by means of thermogravimetry (TG), differential thermal analysis (DTA) and derivative thermogravimetry (DTG). The exclusion of methanol, hydrolysis of benzoyl ester and methyl ketone groups in *lower rim*, and decomposition of azo groups in *upper rim* have occurred during thermal analysis, consecutively. The thermal decomposition degrees amount of volatile pyrolysis products were determined in air atmosphere using TG, DTA and DTG curves. In conclusion, the thermal analyses of azocalix[4]arenes demonstrated that its stability depends on the substituted groups and their positions in the calix[4]arene structure.

Keywords Calix[*n*]arene · Azocalix[4]arene · TG/DTA · Thermal stability

Introduction

Calix[*n*]arenes are a readily available and important class of macrocycles in supramolecular chemistry. Numerous potential applications of calixarene derivatives such as specific ligands for cations, anions and host of neutral compounds have been reported previously [1–4]. Functional groups are introduced into the existing calix[*n*]arene framework by a functionalized method either in the "*lower rim*" (the oxygen-position of the phenolic moieties) or the "*upper rim*" (the *p*-position of the aromatic nuclei) [5]. Literature surveys show that the majority of studies have not only focused on the thermal behaviour but also concentrated on functionalization [6].

Azocalix[*n*]arenes, generated by the insertion of nitrogen atoms into the *p*-position unit of the calix[*n*]arene structure, have several isomers based on the positions of the nitrogen atoms and its ring size. The first reported calixarene diazo coupling has involved the reaction of *p*-nitrobenzenediazonium tetrafluoroborate with calix[4]arene [7]. Previously, thermal behaviour of azocalixarenes with functionalized groups located at the *upper rim* have been studied by our group with using thermogravimetry (TG), differential thermal analysis (DTA) and derivative thermogravimetry (DTG) methods [8, 9].

Thermal analysis plays important role in structure and stability studies of both organic and inorganic compounds [10–12]. TG analysis is a valuable tool for the analysis of inclusion compounds of calixarenes, providing a comprehensive method to analyze trends of molecular forces involved in the complexation, quantitatively. The azocalix[*n*]arene molecular complexes form small molecules with variable stoichiometries in solid state. Increasing temperature promotes a reverse acid–base reaction, with the loss of small molecule of the solid, and the temperature of leaving of the small molecule decreases for longest chain small molecules [8].

Schatz et al. [13] reported the solid state inclusion of various organic solvent molecules in *p*-*tert*-butylcalix[4 and 6]arene. Formerly, it has been reported that ammonium cation complexes of *p*-*tert*-butylcalix[6]arenes were synthesized and characterized [14]. This observation is also reported by Radius and coworkers [15], who prepared calix[4]arene-supported iron(III) complexes.

Complexes of amines with calixresorcinarenes are formed in solution, with a complementary fit of the sizes of

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the calix cavity by secondary and tertiary amines. Calixresorcinarene forms complexes with amines with stoichiometry 1:2 in the solid state [16]. There are few examples of structures of decomposition of azocalixarenes/calixarenes [17, 18] or azocalixarene metal complexes determined by X-ray crystallography [19] and they show a variable positions of the metal cation, which in some complexes bind the cavity by interactions with the clouds and others only by hydrogen bonding to the phenolic oxygens.

Recently, synthesis of various kinds of calix[4]arene derivatives [20] and their complexes [21], polymeric calix[*n*]arene derivatives [22], azocalix[*n*]arenes [23] and theoretical studies [24] have been mainly reported by our group. We have examined the selective extraction of Fe^{3+} ion from aqueous phase into the organic phase as well as the liquid–liquid extraction of transition metal ions using diazo-coupled calix[*n*]arenes [25]. However, there is still an important need for systems those can exhibit colour changes with ionic or molecular interactions.

In this study, we mainly look into the development of a new class of chromogenic azocalix[4]arene dyes. This study focuses on thermal behaviour and thermal decomposition of sixteen diazo-coupled *mono*- and *di*-azo substituted calix[4]arenes (**A1**–**A8** and **B1**–**B8**) (Fig. 1). There has been few number of reports on the thermal decomposition analysis of azocalix[4]arene-based compounds so far.

Experimental

All the reagents were purchased from Merck or Carlo-Erba Company and used without further purification.

p-*tert*-Butylcalix[4]arene, calix[4]arene, [25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(2-nitrophenylazo)calix[4]arene (**A1**), 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(3-nitrophenylazo)calix[4]arene (**A2**), 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(4-nitrophenylazo)calix[4]arene (**A3**), 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(4-phenylazophenylazo)calix[4]arene (**A4**), 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(3-chlorophenylazo) calix[4]arene (**A5**), 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(4-chlorophenylazo) calix[4]arene (**A6**), 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(2-methylphenylazo)calix[4]arene (**A7**) and 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(4-methylphenylazo)calix[4]arene (**A8**)] and [25,27-diacetonyloxy-26,28-dihydroxy-11,23-di-(*tert*-butyl)-5,17-(2-nitrophenylazo)calix[4]arene (**B1**), 25,27-diacetonyl oxy-26,28-dihydroxy-11,23-di-(*tert*-butyl)-5,17-(3-nitrophenylazo)calix[4]arene (**B2**), 25,27-diacetonyloxy-26,28-dihydroxy-11,23-di-(*tert*-butyl)-5,17-(4-nitrophenylazo)calix[4]arene (**B3**), 25,27-diacetonyloxy-26,28-dihydroxy-11,23-di-(*tert*-butyl)-5,17-(4-phenylazophenylazo)calix[4]arene (**B4**), 25,27-diacetonyloxy-26,28-dihydroxy-11,23-di-(*tert*-butyl)-5,17-(3-chlorophenylazo)calix[4]arene (**B5**), 25,27-diacetonyloxy-26,28-dihydroxy-11,23-di-(*tert*-butyl)-5,17-(4-chlorophenylazo)calix[4]arene (**B6**), 25,27-diacetonyloxy-26,28-dihydroxy-11,23-di-(*tert*-butyl)-5,17-(2-methylphenylazo) calix[4]arene (**B7**) and 25,27-diacetonyloxy-26,28-dihydroxy-11,23-di-(*tert*-butyl)-5,17-(4-methylphenylazo)calix[4]arene (**B8**)] were synthesized as described in a previously reported method. The obtained compounds are purified by crystallization using DMF-H_2O and analyzed, consecutively [26–29].

Instrumental

Thermo-analytical TG, DTG and DTA curves were obtained simultaneously using a Shimadzu DTG-60H thermal analyzer. The measurements were carried out in flowing air atmosphere with a flow rate of 25 mL min^{-1} and the temperature range of 298–1123 K in platinum crucible. The heating rate was 10 K min^{-1} and the sample masses were in the range of 3–5 mg. Highly sintered α-Al_2O_3 was used as the reference material.

Results and discussion

Thermal analysis plays an important role in studying structure and stability of calix[*n*]arenes. The applicability of some azocalix[*n*]arenes for special uses and their thermal stability determination are also very important. Substitution of azocalix[*n*]arene with various ligands on *para*-position expands the size of the hydrophobic cavity and

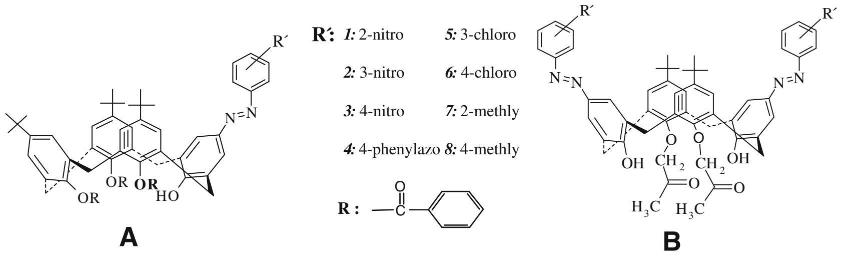

Fig. 1 Diazo-coupled *mono*- and *di*-azocalix[4]arene derivatives (**A1**–**A8** and **B1**–**B8**)

provides additional contact points for molecular interactions between host and guest. The heat resistance at elevated temperatures is one of the main properties of azocalix[*n*]arenes which enable their high temperature applications such as dyeing and chromoionophore. They are also used in high technology areas such as sensors and receptors.

The main focus of this work was thermal analysis of new azocalix[4]arenes. The starting material *p*-*tert*-butylcalix[4]arene and calix[4]arene were synthesized according to the reported methods [23, 24]. On the basis of our previous experience [25, 28], azocalix[4]arene derivatives have been synthesized from calix[4]arene by diazo coupling with the corresponding aromatic amines.

In the experiments, the selected azocalix[4]arenes derivatives (**A1**–**A8** and **B1**–**B8**) were placed into dried Schlenk tube against a dry air flow at atmospheric pressure. These compounds were then heated to the desired temperature under static air.

A simple and effective method for the investigation of inclusion phenomena is TG analysis. It is especially convenient for small, volatile organic guest molecules. A typical curve obtained by TG of azocalix[*n*]arene-solvent complexes is shown in Fig. 2. The corresponding host–guest ratio can easily be calculated from the loss of weight Δm (%). Furthermore, the differences between T_1 and the boiling point of the solvent, represents a qualitative measure for the binding strength of the host–guest molecule in the crystal lattice [10]. All gravimetric results are summarized in Table 1.

Generally, the profile of the TG analysis of azocalix[4]arene derivatives (**A1**–**A8** and **B1**–**B8**) shows weight losses between 343, 473–633 and 673–873 K, corresponding to exclusion of methanol, hydrolysis of benzoyl ester and methyl ketone groups in *lower rim*, and decomposition of azo groups in *upper rim*, respectively. All results were given in Table 1. The weight loss data allow the determination of the stoichiometric ratio between azocalix[4]arenes and methanol.

Inital decomposition step, which occurred approximately at 343 K, includes removal of methanol from tribenzoyl *mono*-azocalix[4]arene derivatives (**A1**–**A8**) (observed mass loss: 3.066, 3.005, 2.899 for **A1**, **A2**, **A3**; theoretical 2.949). Second decomposition step which occurred between 593 and 623 K includes decomposition of tribenzoyl and *tert*-butyl groups (observed mass loss: 29.725, 30.384, 29.607 for **A1**, **A2**, **A3**; theoretical 29.217) and finally rest of the structure decomposes approximately at 773 K (observed mass loss: 71.151, 69.115, 68.599 for **A1**, **A2**, **A3**; theoretical 67.834).

Azocalix[4]arenes (**B1**–**B3**) show the same decomposition behaviour which is represented in Fig. 3. The removal of methanol groups occurred (observed mass loss: 3.261, 3.282, 2.266 for **B1**, **B2**, **B3**; theoretical 3.268), is followed by transformation of *di*-azocalix[4]arenes into calix[4]arenes with decomposition of azo groups (observed mass loss: 30.435, 30.397, 30.428 for **B1**, **B2**, **B3**; theoretical 30.437). Finally rest of the structure is decomposed (observed mass loss: 69.622, 56.908, 56.826 for **B1**, **B2**, **B3**; theoretical 56.894). This information is compatible with our published results [9].

The DTA thermograms in Figs. 2 and 3 indicate that decomposition steps occur at 343, 573 and 773 K, respectively. In particular, it is a well-known fact that the azocalix[4]arene derivatives exhibit interesting phase polymorphism and large thermal hysteresis of phase I ↔ phase II transition, which is connected with the room temperature (←) or set in motion (→) the fast reorientation of a characteristic part of the CH_3OH groups. In the first two phases of the azocalix[4]arenes all CH_3OH solvents reorientate fastly. On the other hand, final decomposition phase of diketone *di*-azocalix[4]arenes (**B1**–**B3**) includes two steps. This refers to *cone* conformation for tribenzoyls and diketone compounds.

The aim of this study is to determine whether the above described picture of the molecular reorientational motions of the azocalix[4]arene derivatives has some correlation with the mechanism of their thermal dealkolation and find out the differences in the thermal decomposition of their dealkolation products.

Azocalix[4]arenes **A4** and **B4** have been the most interesting compounds of all. These compounds have been subjects of interest in our previous solvent extraction and UV absorption (keto-enol tautomerism) studies. The existence of

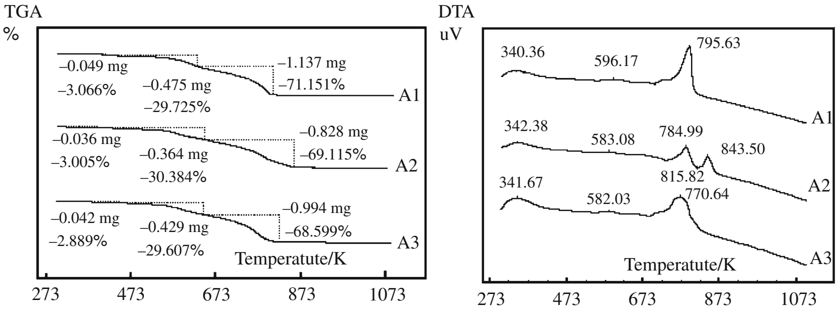

Fig. 2 The TG and DTA curves of azocalix[4]arenes **A1**–**A3** in air atmosphere

Table 1 The thermoanalytical results obtained from TG and DTA curves

Compounds	T_i–T_f/K	T_{peak}/K	% Mass loss^{exp}	% Mass loss^{theo}	Removed groups
A1	313–414	340.36	3.066	2.949	1 mol CH_3OH
	414–630	596.17	29.725	29.217	Azo substituted part + 3 *tert*-butyl
	630–808	795.63	71.151	67.834	Rest of structure decomposes
A2	313–392	342.38	3.005	2.949	1 mol CH_3OH
	392–646	582.48	30.384	29.217	Azo substituted part + 3 *tert*-butyl
	646–858	784.99	69.115	67.834	Rest of structure decomposes
A3	313–446	341.67	2.899	2.949	1 mol CH_3OH
	446–645	582.03	29.607	29.217	Azo substituted part + 3 *tert*-butyl
	645–823	770.64	68.559	67.834	Rest of structure decomposes
A4	313–446	413.33	2.721	2.792	1 mol CH_3OH
	446–652	578.71	33.223	33.153	Azo substituted part + 3 *tert*-butyl
	652–864	782.06	64.056	64.055	Rest of structure decomposes
A5	313–432	341.90	2.981	2.968	1 mol CH_3OH
	432–593	571.83	12.244	12.987	Azo substituted part
	593–715	720.52	33.681	33.673	O–C=O part of benzene
	715–821	812.99	54.571	50.372	Rest of structure decomposes
A6	303–433	340.72	2.939	2.968	1 mol CH_3OH
	433–639	568.99	29.262	29.654	O–C=O part of benzene
	639–835	802.17	72.632	67.378	Rest of structure decomposes
A7	313–420	345.05	1.704	1.724	1 mol H_2O
	420–635	–	30.470	30.172	O–C=O part of benzene
	635–833	798.77	74.915	68.104	Rest of structure decomposes
A8	313–387	341.41	1.749	1.724	1 mol H_2O
	387–643	623.93	30.109	30.172	O–C=O part of benzene
	643–843	777.70	73.005	68.104	Rest of structure decomposes
B1	313–428	341.06	3.261	3.268	1 mol CH_3OH
	428–593	562.38	30.435	30.437	Azo substituted part
	593–825	736.30	69.622	66.295	Two phase decomposition without clear separation
	825–873	785.15			
B2	313–420	340.05	3.282	3.268	1 mol CH_3OH
	420–645	560.92	30.397	30.437	Azo substituted part
	645–769	746.44	56.908	56.894	Two phase decomposition without clear separation
	769–838	819.48			
B3	313–395	340.78	3.266	3.268	1 mol CH_3OH
	395–631	607.31	30.438	30.437	Azo substituted part
	631–773	731.75	56.826	56.894	Two phase decomposition without clear separation
	773–869	826.69	14.500	9.401	
B4	313–393	344.96	2.929	2.917	1 mol CH_3OH
	393–684	569.54	38.242	38.286	Azo substituted part
	684–846	815.32	67.372	58.797	Rest of structure decomposes
B5	313–412	342.85	3.331	3.313	1 mol CH_3OH
	412–596	447.83	28.845	28.985	Azo substituted part
	596–814	778.35	72.573	67.702	Rest of structure decomposes
B6	313–409	340.03	3.343	3.313	1 mol CH_3OH
	409–636	721.95	29.027	28.985	Azo substituted part
	636–933	797.88	73.708	67.702	Rest of structure decomposes
B7	313–489		3.370	3.382	1 mol CH_3OH
	489–652		25.313	25.369	Azo substituted part
	652–838		78.840	71.249	Rest of structure decomposes
B8	451–649		25.394	25.369	Azo substituted part
	649–840		80.836	73.004	Rest of structure decompose

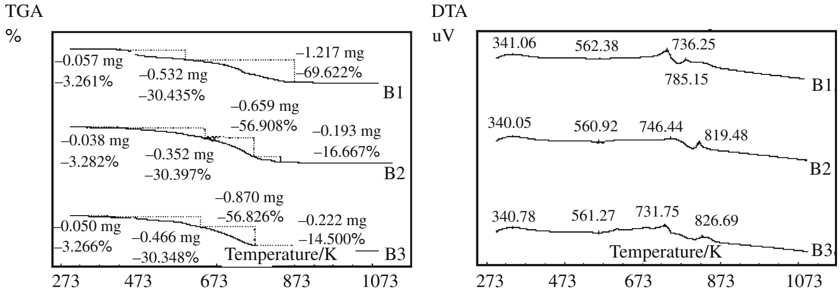

Fig. 3 The TG and DTA curves of azocalix[4]arenes **B1**–**B3** in air atmosphere

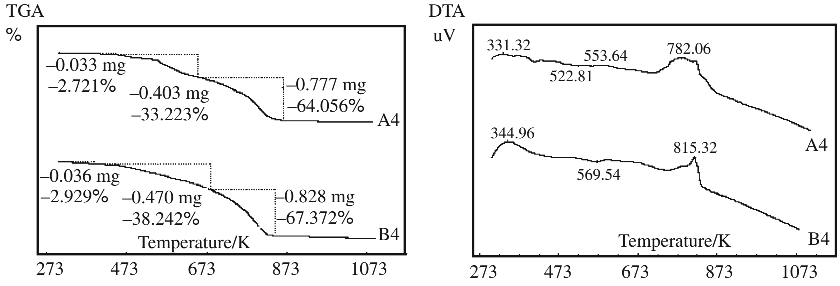

Fig. 4 The TG and DTA curves of azocalix[4]arenes **A4** and **B4** in air atmosphere

diazo groups in their structures helps them to increase conjugation and exhibit interesting properties. Existence of both endothermic and exothermic peaks between 473 and 773 K in thermograms of compounds **A4** and **B4** refers decomposition of azo group separately. On the other hand, they are showed that they excluded parts form host–guest complexes with polymorphism and thermal hysterics of azocalix[4]arene. Both of them decompose in three steps like the others. The occurrence of endothermic peaks with exothermic ones in DTA refers to intermolecular reconfiguration during decomposition (Fig. 4).

Thermogravimetric methods were determined the nature of included solvent molecules. All intercalary guests were identified and impurities by other solvent molecules could be excluded by this method. In all cases only one type of guest molecule could be detected. All of calix[4]arenes used in this study showed methanol or water removal at 343 K confirming the literature [10].

A5–**A6** and **B5**–**B6** show the same decomposition behaviour. Both TG and DTA thermograms contain resemblances with respect to each other (Fig. 5). While the DTA thermograms of compounds **A5** and **A6** show single

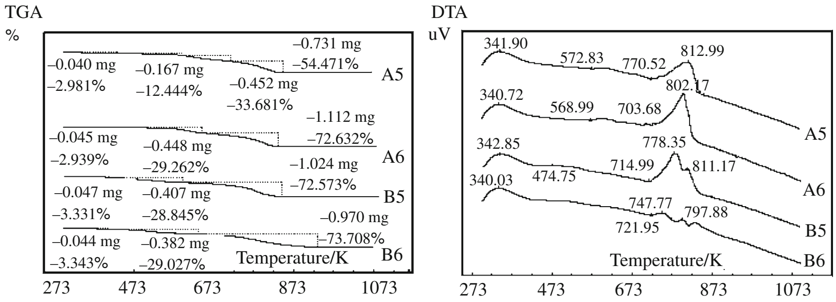

Fig. 5 The TG and DTA curves of azocalix[4]arenes **A5**–**A6** and **B5**–**B6** in air atmosphere

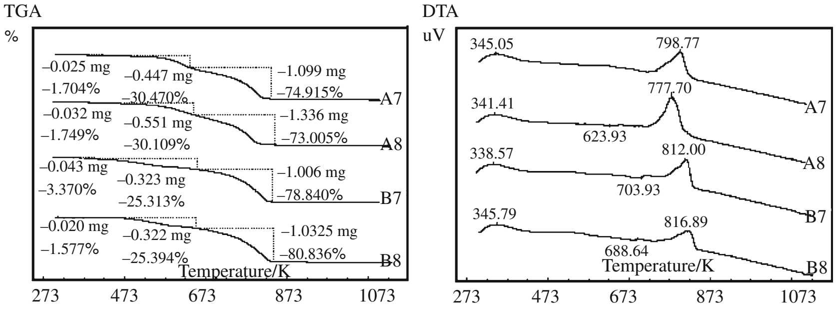

Fig. 6 The TG and DTA curves of azocalix[4]arenes **A7**–**A8** and **B7**–**B8** in air atmosphere

exothermic peak, those of compounds **B5** and **B6** show double exothermic peaks.

Azocalix[4]arenes **A7**–**A8** do not resemble to azocalix[4]arenes **B7**–**B8** as a host molecule for small organic solvent molecules (Fig. 6). The ΔT_{bp} values are usually lower than those obtained for azocalix[4]arene and the host–guest ratios cannot be explained by the sole existence of a combination of complexed and empty host azocalix[4]arenes **A7**–**A8**. Behaviour of solvent molecules on interstitial positions in the crystal lattice indicates that this is a non-specific complexation. TG analysis of azocalix[*n*]arene-solvent complexes gives information of intramolecular forces involved. All these findings are in agreement with the data from similar clathrates which have already been identified by X-ray diffraction analysis in literature [10].

Conclusions

In conclusion, decomposition steps were summarized as removal of methanol, hydrolysis of benzoyl ester and methyl ketone groups in *lower rim*, and decomposition of azo groups in *upper rim* has occurred during thermal analysis, consecutively. Existence of both endothermic and exothermic peaks in DTA diagrams of compounds **A4** and **B4** refer to separate decomposition of each azo group. The theoretical and experimental mass loss percentages obtained from these decomposition stages are in agreement. The thermal analysis of azocalix[4]arene demonstrated that the stability of the calix[4]arene depends on substituted groups and their position in the calix[*n*]arene structure.

The azocalix[4]arene forms stable complexes with small organic guests in the solid state and the resulting host–guest ratios can be easily determined by TG. The very strong binding of CH_3OH inside the cavity is not fully understood yet. Structural ideas based on TG analysis were supported by ^{1}H-NMR in the literature [25]. Azocalix[4]arene generally forms *endo* complexation with CH_3OH. Azocalix[4]arene–CH_3OH complex seems to have single CH_3OH molecule located on interstitial positions and one side the cavity, the oxygen atom pointing outside. As expected, azocalix[*n*]arene form simple *endo* complexes.

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References

1. Gutsche CD. Calixarene revisited. Cambridge: The Royal Society of Chemistry; 1998.
2. Abraham W. Inclusion of organic cations by calix[*n*]arenes. J Incl Phenom Macrocycl Chem. 2002;43:159–74.
3. Ikeda A, Shinkai S. Novel cavity design using calix[*n*]arene skeletons: toward molecular recognition and metal binding. Chem Rev. 1997;97:1713–34.
4. Yilmaz M. In: Cheremisinoff NP, editor. Handbook of engineering polymeric materials. New York: Marcel Dekker; 1997.
5. Dhawan B, Chen S-I, Gutsche CD. Calixarenes. 19. Studies of the formation of calixarenes via condensation of para-alkylphenols and formaldehyde. Macromol Chem. 1987;188:921–50.
6. Masuda Y, Zhang Y, Yan C, Li BJ. Synthesis and characterization of scandium(III) complexes with *p*-tert-butylcalix[*n*]arenes ($n = 4, 6, 8$). Alloys Compd. 1998;275:872–6.
7. Shinkai S, Araki K, Shibata J, Manabe O. Autoaccelerative diazo coupling with calix[4]arene—unusual co-operativity of the calixarene hydroxy-groups. J Chem Soc Perkin Trans. 1989;1(1):195–6.
8. Deligöz H. Azocalixarenes: synthesis, characterization, complexation, extraction, absorption properties and thermal behaviours. J Incl Phenom Macrocycl Chem. 2006;55:197–218.
9. Deligöz H, Özen Ö, Koyundereli Çilgi G, Cetişli H. A study on the thermal behaviours of parent calix[4]arenes and some azocalix[4]arene derivatives. Thermochim Acta. 2005;426(1–2):33–8.
10. Refat MS. Synthesis, spectroscopic characterization, thermal, and photostability studies of 2-(2′-hydroxy-5′-phenyl)-5-aminobenzotriazole complexes. J Therm Anal Calorim. 2010;102:1095–103.
11. Sumar Ristovic VT, Minic MD, Poleti D, Miodragovic Z, Miodragovic D, Andelkovic KK. Thermal stability and degradation of Co(II), Cd(II), and Zn(II) complexes with N-benzyloxycarbonylglycinato ligand. J Therm Anal Calorim. 2010;102:83–90.
12. Mojumdar SC, Simon P, Krusikova A. [1]Benzofuro[3,2-c]pyridine synthesis and coordination reactions. J Therm Anal Calorim. 2009;96:103–9.
13. Schatz J, Schildbach F, Lentz A, Rastatter S. Thermal gravimetry, mass spectrometry and solid-state C-13 NMR spectroscopy—simple and efficient methods to characterize the inclusion behaviour of *p*-tert-butylcalix[*n*]arenes. J Chem Soc Perkin Trans. 1998;2:75–7.
14. Lazarotto M, Nachtigall FF, Schnitzler E, Castellano EE. Thermogravimetric analysis of supramolecular complexes of *p*-tert-butylcalix[6]arene and ammonium cations: crystal structure of diethylammonium complex. Thermochim Acta. 2005;429:111–7.
15. Zeller J, Koenig S, Radius U. Synthesis and structural analysis of calix[4]arene-supported iron(III) complexes. Inorg Chim Acta. 2004;357:1813–21.
16. Utzig E, Pietraszkiewicz O, Pietraszkiewicz M. Thermal analysis of calix[4]resorcinarene complexes with secondary and tertiary amines. J Therm Anal Calorim. 2004;78:973–80.
17. Desroches C, Parola S, Vocanson F, Ehlinger N, Miele P, Lamartine R, Bouix J, Eriksson A, Lindgren M, Lopes C. Synthesis, characterization and optical power limiting behaviour of phenylazo- and 4-nitrophenylazo-tetrahydroxytetrathiacalix[4]arene. J Mater Chem. 2001;11:3014–7.
18. Ashram M, Al-Ghezawi N, Awaad IA, Asman G. Synthesis and physical studies of polycarbonate of *p*-tert-butylcalix[4]arene: a highly selective receptor for Na^+. Turk J Chem. 2009;33:647–56.
19. Liu C, Luo F, Bi Y, Liao W, Zhang H. A zinc/*p*-sulfonatocalix[4]arene/phenanthroline supramolecular compound with novel $(H_2O)_{10}$ water clusters. J Mol Struct. 2008;888:313–7.
20. Deligöz H, Ercan N. The synthesis of some new derivatives of calix[4]arene containing azo groups. Tetrahedron. 2002;58:2881–4.
21. Deligöz H. The synthesis of sodium and potassium complexes of two calix[4]arene derivatives. J Incl Phenom Macrocycl Chem. 2001;39:123–5.
22. Deligöz H, Yilmaz M. Selective complexation of Na^+ by polymeric calix[4]arene tetraesters. J Polym Sci A Polym Chem. 1995;33:2851–3.

23. Şener I, Karci F, Kiliç E, Deligöz H. Azocalixarenes. 3: Synthesis and investigation of the absorption spectra of hetarylazo disperse dyes derived from calix[4]arene. Dyes Pigm. 2004;62:141–8.
24. Kara I, Kart HH, Kolsuz N, Karakuş ÖÖ, Deligöz H. Ab initio studies of NMR chemical shifts for calix[4]arene and its derivatives. Struct Chem. 2009;20:113–9.
25. Deligöz H, Ak MS. Azocalixarenes. 6: Synthesis, complexation, extraction and thermal behaviour of four new azocalix[4]arenes. J Incl Phenom Macrocycl Chem. 2007;59:115–23.
26. Karakuş ÖÖ, Deligöz H. Azocalixarenes.7: Synthesis and study of the absorption properties of novel mono-azo substituted chromogenic calix[4]arenes. Turk J Chem. 2010;35:87–98.
27. Karakuş ÖÖ, Deligöz H. Azocalixarenes.8: Synthesis and investigation of the absorption spectra of di-substituted azocalix[4]arenes containing chromogenic groups. J Incl Phenom Macrocycl Chem. 2008;61:289–96.
28. Gutsche CD, Iqbal M. *para-tert*-Butylcalıx[4]arene. Org Synth. 1990;68:234–7.
29. Gutsche CD, Iqbal M, Stewart D. Calixarenes. 19. Syntheses procedures for *p*-tert-butylcalix[4]arene. J Org Chem. 1986;51:742–5.