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A study on the thermal behaviours of parent calix[4]arenes and some azocalix[4]arene derivatives

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Abstract

Thermal behaviours of two parents calix[4]arene (**1**–**2**) and three azocalix[4]arene derivatives (**3**–**5**) containing upper rim functionalized groups such as *n*-butyl, phenylazo and heterocyclic thiazol were investigated by means of thermogravimetry (TG), differential thermal analysis (DTA) and differential thermogravimetry (DTG). The thermal decomposition points and amounts of volatile pyrolysis products were determined in nitrogen and air atmosphere using TG, DTA and DTG curves. In the present study, the thermal analysis of azocalix[4]arenes demonstrated that the stability of the calix[4]arene depends on substituted groups and their position in the calix[4]arene structure.

Keywords: Calixarene; Azocalix[4]arene; Thermal analysis; TG; DTA

1. Introduction

In recent years, there has been an increased interest in the construction and designing of macromolecules specific for the selective recognition of small species such as cations, anions and neutral molecules. Calix[*n*]arenes, macrocyclic phenol–formaldehyde oligomers are easily synthesized by "*one-pot*" procedures [1,2]. Among them calix[4]arenes have proved to be very useful building blocks for synthetic dye compounds [3] and selective metal extraction [4].

It is well known that most of the functional groups are not able to be incorporated into calixarenes by a direct condensation process. Therefore, the functional groups are introduced into the existing calixarene framework by a functionalized method either in the "*lower rim*" (the oxygen-position of the phenolic moieties) or in the "*upper rim*" (the p-position of the aromatic nuclei) [5]. Since, literature surveys show that the majority of studies have not only a few concentrating on the thermal behaviours but also studied concentrated on functionalization [6].

Thermal analysis plays an important role in the study of the structure and stability of calixarenes. The applicability of some azocalix[*n*]arenes for special uses and determining the thermal stabilities of them are also very important. The resistance to heat at elevated temperatures is one of the main properties required of dyes used in high temperature processes such as the dyeing of textile fibers, ink-jet printing and photocopying and in high technology areas such as lasers and electro-optical devices [7,8].

Calixarene chemistry has developed new synthetic methods directed to research areas such as host–guest chemistry, molecular and ionic recognition, supramolecular catalysis, self-organization, aggregation, signal transfer, allosteric effects, etc. Literature on calixarene with upper rim functionalized groups such as azo groups, heterocyclic groups is scarce. Previously Nomura et al., described compounds containing azo groups which are of interest because of their properties of binding sites for metals or of dye chromophores. They reported the synthesis of a calix[6]arene derivative containing

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azo groups and its binding properties for metal ions [9]. Azo coupling reactions of calix[4]arene were studied by Morita et al. [10]. The synthesis of some azocalix[*n*]arene containing these groups has been reported in our previously studies [11–16]. The results of the thermal analysis of these azocalix[*n*]arene can be used to obtain useful information about their thermal stability and also to determine the temperature range in which they can be used without changes in their composition, colour and properties [17].

In this study we report the thermal behaviours and the amount of volatile pyrolysis products of parent calix[4]arenes (**1**–**2**) and some azocalix[4]arenes (**3**–**5**) which have *n*-butyl, phenylazo and heterocyclic thiazol groups.

2. Experimental

All the reagents used were purchased from Merck or Carlo-Erba Company and are chemically pure.

Calix[4]arene [18] (**1**), *p*-*tert*-butylcalix[4]arene [19] (**2**), *p*-(4-*n*-butylphenylazo)calix[4] arene [15] (**3**), *p*-(4-phenylazophenylazo)calix[4]arene [15] (**4**) and *p*-(*N*′-2-thiazol-2-ylsulfanylazo) calix[4]arene [15] (**5**) were synthesized as described in a previously reported method.

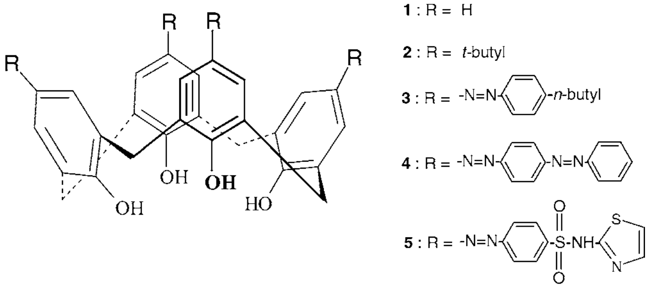
2.1. Instrumental

Thermo-analytical TG, DTG and DTA curves were obtained simultaneously by using a Shimadzu DTG-60H Thermal Analyzer. The measurements were carried out in flowing nitrogen and air atmosphere with a flow rate of 25 mL min^{-1} and the temperature range of 25–850 °C in platinum crucible. The heating rate was 10 °C 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.

3. Results and discussion

In the light of our previous experience, the metal binding properties of azocalix[*n*]arenes were investigated and showed high selectivity for Ag^+, Hg^+ and Hg^{2+} ions, promoting us to elaborate on its structure so that it could be in corporated into different types of calixarenes. Thus, the main focus of this work was the thermal behaviours of azocalix[4]arene that would be easily accessible, have an effective binding character for a particular set of cations, and could be useful for multiple applications such as the dyeing of textile fibers, ink-jet printing, photocopying, lasers and electro-optical devices and industrial process analysis. To achieve the desired goal, we have occurred to synthesize calix[4]arene **1**–**5**. With the present work, we extended our previous studies by calix[4]arene with different aniline derivatives.

All thermal analysis measurements in this work were performed under exactly the same experimental conditions. Five calix[4]arene different compounds (**1**–**5**) involving two different diazo groups in *upper rim* were investigated. The structures of the azocalix[4]arene which were synthesized by azocoupling diazonium salts of calix[4]arenes, are shown that in Scheme 1.



Scheme 1. The structures of the calix[4]arenes and their derivatives.

Table 1
The thermoanalytical results obtained from TG, DTA and DTG curves

Compounds	Stage	Air atmosphere		N_2 atmosphere	
		Temperature range (°C)	DTA_{max} (°C)	Temperature range (°C)	DTA_{max} (°C)
$C_{28}H_{24}O_4$ **1**	1	155–271	334.52	158–250	334.21
	2	298–380	521.52	281–375	517.40
	3	433–515	–	436–503	541.14
$C_{44}H_{56}O_4$ **2**	1	216–260	335.04	215–260	338.39
	2	266–345	–	266–345	566.58
	3	361–847	–	348–625	–
$C_{69}H_{76}N_8O_5$ **3**	1	250–300	284.73	250–299	278.34
	2	312–631	531.48	312–852	–
	3		–		–
$C_{77}H_{60}O_5N_{16}$ **4**	1	189–230	208.29	183–220	210.03
	2	254–385	534.32	253–371	507.37
	3	412–645	–	378–841	
$C_{64}H_{48}O_{12}N_{16}S_8$ **5**	1	253–371	307.20	249–284	307.05
	2	371–407	500.71	285–375	372.57
	3	418–842	564.73	514–844	411.21

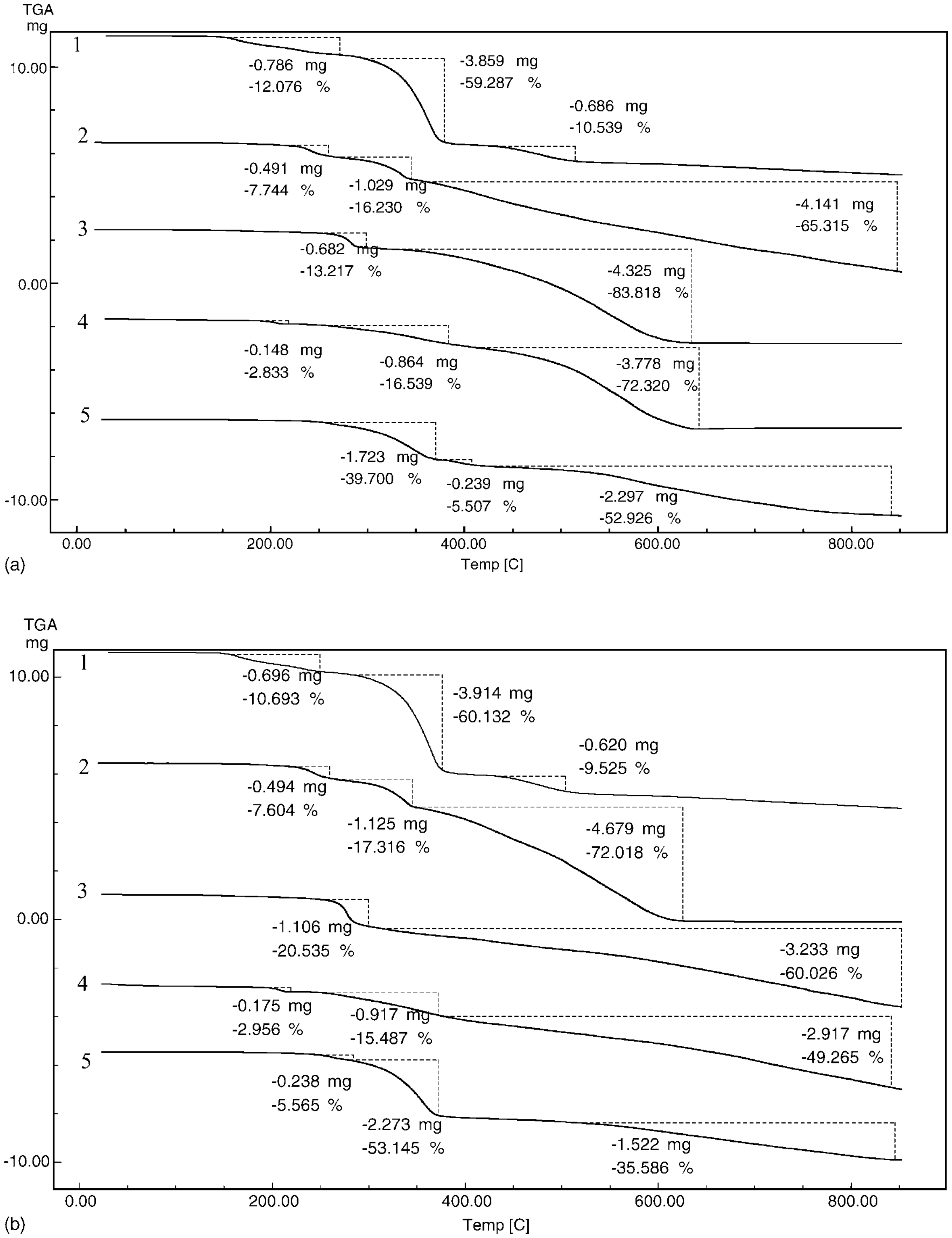


Fig. 1. The TG curves of calix[4]arenes **1**–**5** in air atmosphere (a) and in N_2 atmosphere (b).

The TG and DTA curves of parent calix[4]arenes (**1**–**2**) and azocalix[4]arenes (**3**–**5**) in flowing nitrogen and air atmosphere are illustrated in Figs. 1 and 2. The amount of volatile pyrolysis products for calix[4]arenes and the thermoanalytical results obtained from TG, DTA curves are also given in Table 1.

The thermal analysis curves for the different samples (parent calix[4]arenes and azocalix[4]arenes) did not show any marked differences of similar experimental conditions but did indicate that the samples were not simply calix[4]arene.

From the TG and DTA curves, the weight losses at the first stage take place at 155 °C by a slow pro-

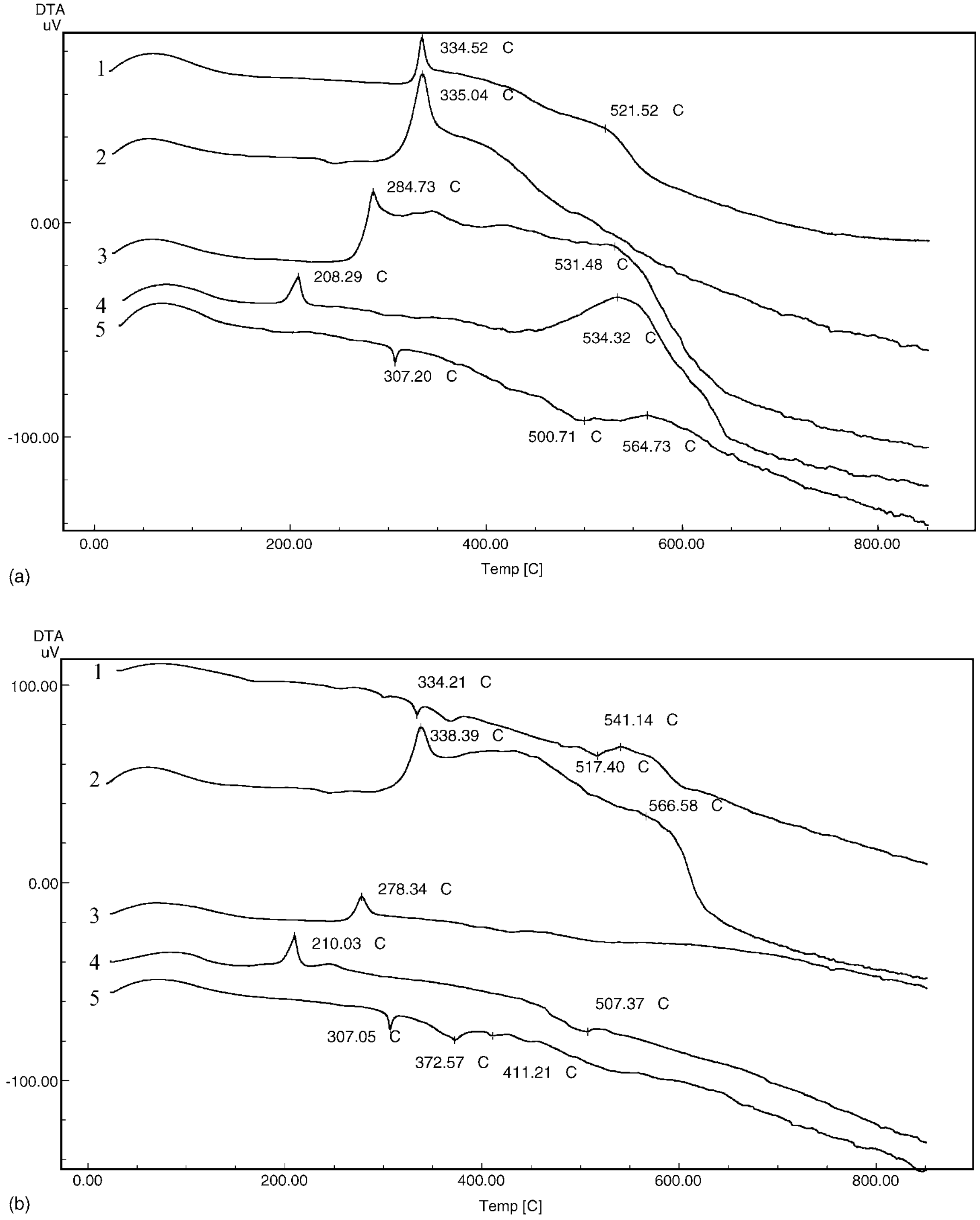


Fig. 2. The DTA curves of calix[4]arenes **1**–**5** in air atmosphere (a) and in N_2 atmosphere (b).

cess, depending on three moles methanol in the structure. Furthermore, the entire anhydrous azocalix[4]arene **3**–**5** give first exothermic peak from 284 to 307 °C, but calix[4]arene **1** is stable to 335 °C because of not having the substituted groups. There are no colour differences between the hydrous and anhydrous azocalix[4]arene. According to these values, the decomposition points of azocalix[4]arene **3**–**5** which contain substituted groups such as *n*-butyl, phenylazo and heterocyclic thiazol groups show considerable differences from 25 to 155 °C relative to calix[4]arene **1**–**2** which does not have substituted calix[4]arene derivatives. In addition, exothermic changes just before the decomposition are observed in two azocalix[4]arenes (**3**–**4**) at 285 and 208 °C, although that process is observed in parallel with the decomposition of calix[4]arene **1**.

As the calix[4]arene **1**, Fig. 2a shows that at 10 °C min^{-1} in air atmosphere, there was no endothermic peak on the DTA but under the same conditions in N_2 atmosphere the endothermic peak was present. According to the authors, an endothermic peak usually appears because of delayed recrystallization. According to these investigators, the parent calix[4]arene loses methanol to form an amorphous product and then loses stream endothermically. In a stream of methanol, this decomposition is repressed because of the recrystallization to calix[4]arene.

It was observed that the azocalix[4]arene investigated do not have the same thermal decomposition stage. For example, all the azocalix[4]arene decompose in at least two or three stages. Although the thermal decomposition mechanism of azo compounds is complex, it basically consists of an aromatic splitting of azo bond in most of the azo compounds [21,22].

From the TG curve of calix[4]arene **1** (Fig. 1) without substituted groups, it is shown that the weight losses occurred between 155–271, 298–380 and 433–515 °C. The temperature range 155–271 °C corresponds to the loss of methanol in the structure, and the other values are the decomposition stages. While the DTA curve of azocalix[4]arene **3** and **4** (Fig. 2a) gives exothermic decomposition peaks at 285 and 208 °C.

As seen from the TG curve, *p-tert*-butylcalix[4]arene **2** decomposes in three stages over the temperature range 216–847 °C. The first decomposition occurs between 216 and 260 °C with a mass loss of 7.74% (theoretical: 7.50%) and the second decomposition starts at 266 °C and ends at 345 °C with a 16.23% mass loss (theoretical: 17.59%); this stage probably corresponds to the mass of *t*-butyl groups. The third decomposition starts at 361 °C.

The TG curve of azocalix[4]arene 3, which is a *n*-butyl derivative, shown in Fig. 1a, illustrates that the removal of three moles of methanol and the formation of the anhydrous azocalix[4]arene **3** took place during the first stage simultaneously. This decomposition stage occurred at 250–300 °C in the first part (Fig. 1a). In the DTA curve of the azocalix[4]arene **3**, the exothermic change was observed near decomposition at 285 °C like azocalix[4]arene **4** (Fig. 2a).

From the TG curve of azocalix[4]arene **3** in N_2 atmosphere (Fig. 1b) it appeared that the sample decomposes over the temperature range 250–299 °C with a mass loss of 20.54% (theoretical: 21.42%). This stage probably corresponds to the mass of *t*-butyl groups.

The thermal behaviour of another synthesized azocalix[4]arene derivative was also studied by DTA. The DTA curves of the azocalix[4]arene **4** in air atmosphere showed a exothermic peak at 534 °C which corresponds to decomposition. The sample decomposes with a mass loss of 16.54% (theoretical: 16.56%). We did not observe any peak after that temperature in the DTA curve, but mass loss was going on in the TG curve.

In the TG profile of azocalix[4]arene **5** in air atmosphere (Fig. 1a) it observed that the sample decomposes over the temperature range 253–371 °C with a mass loss of 39.70% (theoretical: 43.81%). This stage probably corresponds to the mass of heterocyclic thiazol groups.

When the thermal analysis of the sample was carried out under nitrogen atmosphere, the exothermic peak was observed at a flow rate of 25 mL min^{-1}. Similar results were found when the sample was analyzed in air atmosphere. Generally the decomposition peaks were endothermic but each exothermic peaks were noted, always accompanied by a very sharp drop in the TG curve, and the weight loss in this region may be significant. The exothermic DTA peak was found to be strongly influenced by the rate at which the samples were atmospheric conditions.

The fact that the slopes of the curves were very close to unity indicates that only one groups is separated from the ligand. A detailed mechanism related to the thermal decomposition process has been reported in the literature [20–22].

4. Conclusion

In the summary, it was concluded from TG and DTA studies that organic calix[4]arene copolymers decompose in two or three stages and compounds melt with simultaneous decomposition. The theoretical and experimental percentage mass losses obtained from these decomposition stages are in good 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. As a result, the TG and DTA studies on azocalix[4]arene **1–5** showed that they can be used for versatile applications in various fields such as textile fibres, which require thermal stability up to 155–254 °C.

References

[1] C.D. Gutsche, Calixarene Revisited, Royal Society of Chemistry, Cambridge, 1998.

[2] M. Yilmaz, Solution state metal complexes of calixarenes and polymeric calixarenes, in: N.P. Cheremisinoff (Ed.), Handbook of Engineering Polymeric Materials, Marcel Dekker, Inc., New York, 1997.

[3] F. Karcı, I. Şener, H. Deligöz, Dyes Pigments 59 (2003) 53.

[4] H. Deligöz, M. Tavasli, M. Yilmaz, J. Polym. Sci. Part A. Polym. Chem. 32 (2961).

[5] B. Dhawan, S.-I. Chen, C.D. Gutsche, Macromol. Chem. 188 (1987) 921.

[6] Y. Masuda, Y. Zhang, C. Yan, B. Li, J. Alloys Compd. 275 (1998) 872.

[7] M. Matsui, A. Sedyohutomo, M. Satoh, Y. Abe, K. Funabiki, H. Muramatsu, K. Shibata, Dyes Pigments 40 (1998) 21.

[8] R. Egli, in: A.T. Peters, H.S. Freeman (Eds.), Color Chemistry the Design and Synthesis of Organic Dyes and Pigments, Elsevier, London, 1991.

[9] E. Nomura, H. Taniguchi, S. Tamura, Chem. Lett. (1989) 1125.

[10] Y. Morita, T. Agawa, E. Nomura, H. Taniguchi, J. Org. Chem. 57 (1992) 3658.

[11] H. Deligöz, H.K. Alpoğuz, H. Çetişli, J.M.S. Pure Appl. Chem. 37 (2000) 407.
[12] H. Deligöz, J. Inclusion Phenom. 39 (2001) 123.
[13] H. Deligöz, Supramol. Chem 15 (2003) 317.
[14] H. Deligöz, H. Çetişli, J. Chem. Res. 10 (2001) 427.
[15] H. Deligöz, N. Ercan, Tetrahedron 58 (2002) 2881.
[16] F. Karcı, I. Şener, H. Deligöz, Dyes Pigments 62 (2004) 133.
[17] G. Simeonov, A. Dragenov, D. Rustschev, J. Therm. Anal. 36 (1990) 721.
[18] C.D. Gutsche, M. Iqbal, D. Stewart, J. Org. Chem. 51 (1986) 742.
[19] C.D. Gutsche, M. Iqbal, Org. Synth. 68 (1990) 234.
[20] K. Vojciechowsky, J. Szodowsky, J. Therm. Anal. 31 (1986) 297.
[21] H. Kocaokutgen, Z. Heren, Turk. J. Chem. 22 (1998) 403.
[22] F. Karipcin, I. Karataş, H.I. Uçan, Turk. J. Chem. 27 (2003) 453.