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The Synthesis of Ester and Ketone Derivatives of Azocalix[4]arene Containing Chromogenic Groups

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Abstract

Azocalix[4]arenes were prepared by linking 4-ethylaniline, 4-*n*-butylaniline, 4-acetamide aniline and 2-aminothiazol to calix[4]arene through a diazo-coupling reaction. A new family of azocalix[4]arenes, **L1–L12**, have been prepared by the incorporation of acetyl, benzoyl, and methyl ketone units to azocalix[4]arene. Characterization of the synthesized compounds was carried using elemental analyses, UV–Vis, IR and ^{1}H NMR spectroscopic studies.

Introduction

Calixarenes are a class of phenolic macrocycles, extensively used as molecular platforms for the synthesis of efficient and selective receptors [1]. Current studies on the synthesis of calixarene derivatives have focused on the development of optical sensors [2], ion-selective electrodes [3], and spectrofluorometric systems [4]. However, there is still an important need for systems that can exhibit color changes due to ionic or molecular interactions. Among reported researchs, azocalixarenes have been mainly studied: calixarenes bridging phenylazo moieties on the upper rim [5] and lower rim [6], double azocalixarenes [7], azo calixcrowns [8]. On the other hand, the incorporation of azocalix[4]arene agents such as aniline derivatives, incorporeted on lower rim of calixarene have a special interest in the complexation behavior towards transition metal cations [9].

Calixarenes, which appeared after crown ethers and cyclodextrins as the third generation of inclusion compounds, have received much attention. Their ability to recognize and discriminate among metal ions is one of their most remarkable features, and this makes them suitable as specific receptors. In recent years, many calixarene derivatives have been synthesized to achieve highly selective ligands for alkali, alkaline earth and transition metal ions [10, 11].

Shimuzu *et al*. [12] synthesized a chromogenic calix[4]arene, which has within the molecule a calix[4]aryl triester moiety as a metal binding site and an azophenol moiety as a coloration site. Diazo coupling reactions of calix[4]arene were studied by Morita *et al*. [13] and Shinkai *et al*. [14] and they described the resulting NMR spectra. In our recent work, we have synthesized a *vic*-dioxime derivative of calix[n]arene and have studied its complexes [15–19], polymeric calix[n]arene derivatives and selective extraction of transition metal cations [20–24].

In the field of our investigations, we are interested in the development of a new class of chromogenic compounds. Thus the aim of the present work was to build molecules constituted of calix[4]arene, which contain both ester (i.e. acetyl and benzoyl) and ketone moiety as a metal binding site and an azophenyl moieties as coloration site. The incorporation of ester and ketone subunits has been chosen here due to its potential abilities for complexing two ions and its solubility properties. This effort led us to the preparation of 12 new diazo coupling calix[4]arenes substituted by ester and ketone subunits 25,26,27,28-tetraacetoxy-*p*-(4-ethylphenylazo) calix[4]arene (**L1**), 25,26,27,28-tetramethyl-*p*-(4-ethylphenylazo)calix[4]arene tetraketone (**L2**), 25,26,27-tribenzoyloxy-28-hydroxy-*p*-(4-ethylphenylazo) calix[4]arene (**L3**), 25,26,27,28-tetraacetoxy-*p*-(4-*n*-butylphenylazo) calix[4]arene (**L4**), 25,26,27,28-tetramethyl-*p*-(4-*n*-butylphenylazo)calix[4]arene tetraketone (**L5**), 25,26,27-tribenzoyloxy-28-hydroxy-*p*-(4-*n*-butylphenylazo)calix[4]arene (**L6**), 25,26,27,28-tetraacetoxy-*p*-(4-acetanilidazo)calix[4] arene (**7**), 25,26,27,28-tetramethyl-*p*-(4-acetanilidazo) calix[4]arene tetraketone (**L8**), 25,26,27-tribenzoyloxy-28-hydroxy-*p*-(4-acetanilidazo)calix[4]arene (**L9**), 25,26,27,28-tetraacetoxy-*p*-(2-thiazolazo)calix[4]arene (**L10**), 25,26,27,28-tetramethyl-*p*-(2-thiazolazo)calix[4]arene tetraketone (**L11**), 25,26,27-tribenzoyloxy-28-hydroxy-*p*-(2-thiazol azo)calix[4]arene (**L12**) (Scheme 1).

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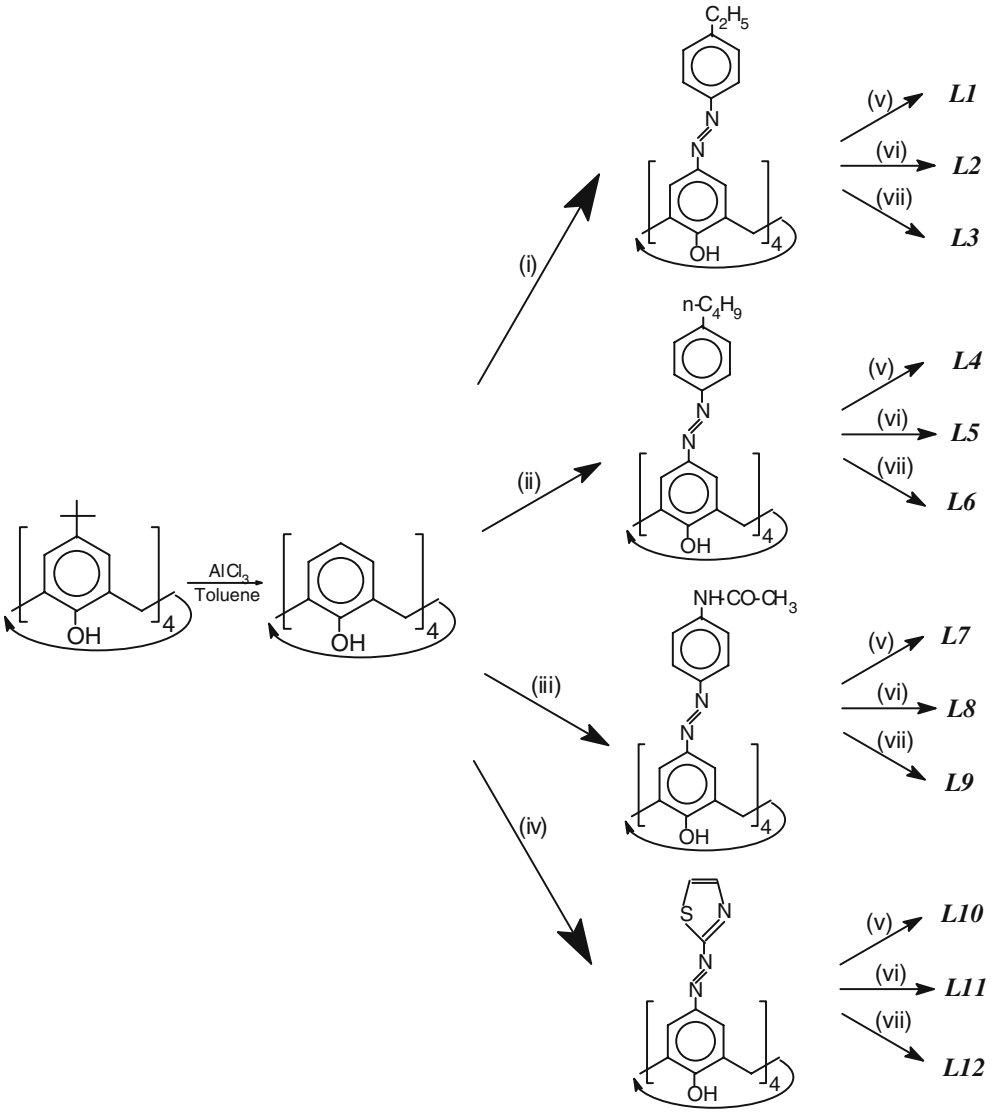
Results and discussion

The preparation of azocalix[4]arene with ester and ketone groups at the *lower rim* is presented in Scheme 1. The synthesis of *p*-tert-butylcalix[4]arene was based on a previous procedure [25]. Calix[4]arene was obtained by debutylation of *p*-tert-butylcalix[4]arene with $AlCl_3$:toluene [26]. Azocalix[4]arenes were synthesized from calix[4]arene and 4-ethyl aniline, 4-*n*-butylaniline, 4-amino acetanilide and 2-aminothiazol (Scheme 1).

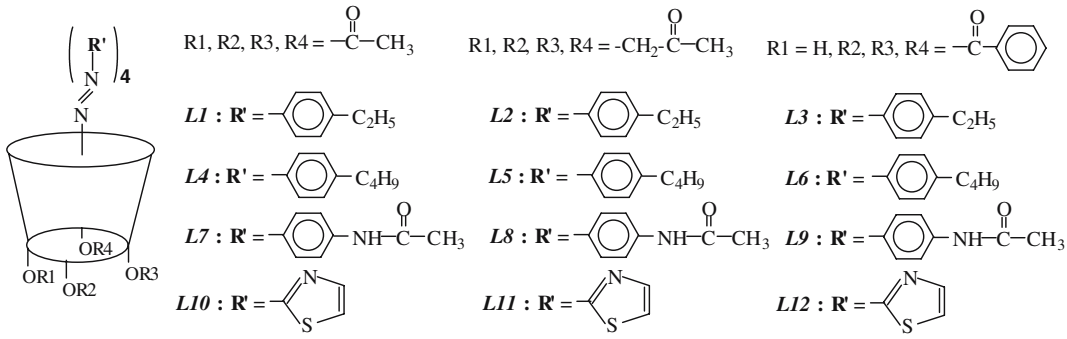
The coupling reaction of calix[4]arene with 4-ethylbenzenediazonium chloride in aqueous THF gave *p*-(4-ethylphenylazo)calix[4]arene with 80% yield. In our recent work, the *p*-(4-*n*-butylphenylazo)calix[4]arene, *p*-(4-acetanilidazo)calix[4]arene and *p*-(2-thiazolazo)calix[4]arene were obtained by the same method in 85, 53 and 68% yield, respectively. Structures were verified by spectroscopic methods and elemental analysis. The diazo (–N = N–) stretching bands of phenylazo groups were observed at 1470–1550 cm^{-1} (Scheme 2).

O-Acetylation of azocalix[4]arenes

It was anticipated that in the presence of aluminium chloride the treatment of the calixarenes with acetyl chloride might yield the *p*-acetyl and *p*-benzoyl compounds. Instead, reaction occurs only on the phenolic functions to yield esters. It was then anticipated that the esters, once formed, might undergo Friedel–Crafts acylation on the benzene rings, but such was not the case. When azocalix[4]arenes are treated with aluminium chloride and acetyl chloride a mixture was obtained that contained the same pair of tetraacetates. The acetylation reaction of azocalix[4]arenes with acetyl chloride in dichloromethane gave 25,26,27,28-tetraacetoxy-*p*-(4-ethylphenylazo)calix[4]arene (**L1**) in 68% yield. The



Scheme 1. Synthesis of Azocalix[4]arenes and their derivatives. Reagents and conditions: (i) 4-ethylaniline, HNO_2, conc. HCl, (ii) 4-*n*-butylaniline, HNO_2, conc. HCl, (iii) 4-acetamide aniline, HNO_2, conc. HCl, (iv) 2-aminothiazol, HNO_2, conc. HCl, and (v) acetyl chloride, $AlCl_3$ (vi) chloroacetone, NaI, K_2CO_3, (vii) benzoylchloride, pyridine.



Scheme 2. Ester and ketone derivatives of azocalix[4]arene.

25,26,27,28-tetraacetoxy-*p*-(4-*n*-butyl phenylazo)calix[4] arene (**L4**), 25,26,27,28-tetraacetoxy-*p*-(4-acetanilidazo) calix[4]arene (**L7**) and 25,26,27,28-tetraacetoxy-*p*-(2-thiazolazo)calix[4]arene (**L10**) were obtained by the same method in 51–56% yield. These yields are similar to those reported for similar compounds [27]. The obtained compounds were purified by crystallization in MeOH–$CHCl_3$ and were then analyzed.

O-Alkylation of azocalix[4]arenes

Initial attempts to produce the methyl ketone series involved alkylation of the calixarenes with chloroacetone, and although azocalixarene derivatives were obtained in this way, the reactions were very slow. We found it more satisfactory to use chloroacetone as the electrophile, and use *in situ* halogen exchange with sodium or potassium iodide in acetone. Production of 25,26,27,28-tetramethyl-*p*-(4-ethylphenylazo)calix[4]arene tetraketone (**L2**) in this fashion was very encouraging *vis-a-vis* ionophoric activity for the alkylation reaction, actually produced a solid sodium/potassium iodide complex as the primary reaction product. It was necessary to heat the complex in water to release the free ketone. The sodium iodide–chloroacetone combination was also used to alkylate azocalix[4]arene, furnishing ketones **L2**, **L5**, **L8** and **L11**, respectively in an uncomplexed state.

The alkylation reaction of azocalix[4]arenes with chloroacetone in dry acetone gave 25,26,27,28-tetramethyl-*p*-(4-ethylphenylazo)calix[4]arene tetraketone (**L2**) in 68% yield. The 25,26,27,28-tetramethyl-*p*-(4-*n*-butylphenylazo)calix[4]arene tetraketone (**L5**), 25,26,27,28-tetramethyl-*p*-(4-acetanilidazo)calix[4]arene tetraketone (**L8**) and 25,26,27,28-tetramethyl-*p*-(2-thiazolazo)calix [4]arene tetraketone (**L11**) were obtained by the same method in 51–56% yield. These yields are in accordance with the literature for similar compounds [27]. The new compounds were purified by crystallization in MeOH–$CHCl_3$.

In these reactions, the base used was K_2CO_3 due to its ability to selectively deprotonate phenolic –OH groups.

O-Benzoylation of azocalix[4]arenes

Azocalix[4]arenes are treated with pyridine and benzoyl chloride, and a mixture containing the same pair of tetrabenzoates was obtained. The benzylation reaction of azocalix[4]arenes with benzoyl chloride in pyridine gave 25,26,27-tribenzoyloxy-28-hydroxy-*p*-(4-ethylphenylazo) calix[4]arene (**L3**) in 68% yield. The 25,26,27-tribenzoyloxy-28-hydroxy-*p*-(4-*n*-butylphenylazo)calix[4] arene (**L6**), 25,26,27-tribenzoyloxy-28-hydroxy-*p*-(4-acetanilidazo)calix[4]arene (**L9**) and 25,26,27-tribenzoyloxy-28-hydroxy-*p*-(2-thiazolazo)calix[4]arene (**L12**) were obtained by the same method in 51–56% yield. These yields are in accordance with the literature for similar compounds [27]. The obtained compounds were purified by crystallization in MeOH–$CHCl_3$.

NMR analysis was used to probe the conformation of these compounds in solution and in the solid state. The ^{1}H NMR data established unequivocally that the calix[4]arene derivatives with *p*-azo substituents, namely, acetyl (**L1**, **L4**, **L7**, **L10**), methyl ketones (**L2**, **L5**, **L8**, **L11**) and benzoyl (**L3**, **L6**, **L9**, **L12**), all posses the *cone* conformation at ordinary temperatures. In addition to the signals unique to the ester/keto group, a signal for the two extremely anisotropic hydrogen atoms ($\Delta\delta \cong 3.0$–5.0) of four equivalent bridging methylene groups. These data discount less symmetrical conformations, and confirm that the four potential ligating side arms in both the ester (for acetyl) and ketone series are preorganized to the extent that they are all mutually *syn* with respect to the calixarene substructure.

Application to these new compounds in field of complexation and solvent extraction are presently under investigation.

Conclusion

Diazo coupling reactions, and acetylation, benzoylation and *O*-alkylation reactions are shown in Scheme 1. We studied the diazo coupling reactions of calix[4]arene with benzendiazonium chloride, 4-ethylaniline, 4-*n*-butylaniline, 4-aminoacetanilide and 2-aminothiazole. This pathway is the most convenient method, and gives the best yield of azocalixarene compounds. Twelve new types of azocalixarene-based receptors with acetyl, benzoyl and methyl ketone groups immersed into a large cavity have been proposed and synthesized. Syntheses of all azocalix[4]arene compounds were achieved by the

combination of the Morita. These reactions proceeded smoothly to produce the corresponding azo compounds in good yield.

The azo groups of these compounds are interesting because they act as metal binding sites as well as chromophores. The incorporation of ester and ketone subunit has been chosen here due to its potential ability to complex multiple mutal ions and its solubility properties. We are currently working with azocalix[4]arene derivatives and in particular their binding properties for metal ions.

Experimental section

All reagents used were purchased from Merck or Carlo-Erba and were chemically pure. Melting points were determined on an Electrothermal IA9100 digital melting point apparatus and are uncorrected. ^{1}H NMR spectra were referenced to tetramethylsilane (TMS) at 0.00 ppm as an internal standard and recorded on a Bruker 200 MHz spectrometer at room temperature (25 ± 1 °C). IR spectra were recorded on a Mattson 1000 FTIR spectrometer as KBr pellets. UV–Vis spectra were obtained on a Shimadzu 1601 UV–Visible recording spectrophotometer. The elemental analyses were performed in the TUBITAK Laboratory (Center of Science and Technology Research of Turkey). Osmometric molecular weight determinations were carried out on a Knauer vapor pressure osmometer at concentrations of ca.10^{-3} mol/L in $CHCl_3$.

Preparation of the ligands

p-tert-Butylcalix[4]arene [25], calix[4]arene [26], *p*-(4-*n*-butylphenylazo)calix[4]arene, *p*-(4-acetanilidazo)calix[4]arene, and *p*-(2-thiazolazo)calix[4]arene [23] were synthesized as described by a previously reported method.

Synthesis of p-(4-ethylphenylazo)calix[4]arene:[13]

A solution of 4-ethylphenyldiazonium chloride, which was prepared from 4-ethyl aniline (6.05 g, 50 mmol), sodium nitrite (2.60 g, 37.67 mmol) and conc. HCl (35 ml) in water (125 ml), was added slowly into a cold (5 °C) solution of calix[4]arene (5.00 g, 11.80 mmol) and sodium acetate trihydrate (20.40 g, 75 mmol) in MeOH–DMF (130 ml, 5:8, v/v) to give a red suspension. After being allowed to stand for 2 h at room temperature, the suspension was acidified with aqueous HCl (150 ml, 0.25%). The mixture was warmed to 60 °C for 30 min to produce in near quantitative yield (9.88 g, 88%) as a reddish solid, which was filtered and washed with water and MeOH. A sample for analysis was obtained as follows: Compound was dissolved in 100 ml of a hot $NaHCO_3$ (4.20 g) solution. To this solution was added activated charcoal (1.00 g). After the charcoal was filtered, the filtrate was cooled (room temperature) and acidified with conc. HCl (1 or 2 ml). The solution was heated (60 °C) again for 30 min and cooled. The resulting solid was filtered, washed with water, and dried. Yield, 8.64 g (77%) as a dark yellow solid, m.p. 206 °C; [Found: C 75.73; H 6.01; N 11.57. $C_{60}H_{56}N_8O_4$ requires C 75.60; H 5.91; N 11.70]. $\lambda_{max}(\epsilon)$: 336 (8970). υ_{max}: 3526, 1457 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C): δ_H: 1.10 (12H, t, –CH_3), 2.30 (8H, m, –CH_2–Me), 3.70–4.00 (8H, d, AB, Ar–CH_2–Ar), 6.90–7.00 (24H, m, Ar–H), 10.10 (4H, s, –OH).

This compound was soluble in EtOH, diethyl ether, acetone, acetic acid, benzene, $CHCl_3$, DMSO and insoluble in water.

Synthesis of 25,26,27,28-tetraacetoxy-p-(4-ethylphenylazo)calix[4]arene [27] *(L1)*

A solution containing 1.60 g (23.97 mmol) of $AlCl_3$ and 3.18 ml (44.76 mmol, 3.51 g) of acetyl chloride in 25 ml of CH_2Cl_2 was slowly added to a solution of 1.76 g (1.85 mmol) of calix[4]arene in 25 ml of CH_2Cl_2 at reflux temperature. After 2 h of reflux the mixture was poured into ice water, and the organic layer was separated and dried over Na_2SO_4. Evaporation of the solvent and recrystallization from MeOH–$CHCl_3$ gave 1.41 g (68%) of the tetraacetate. m.p. 155 °C; [Found: C 71.98; H 6.19; N 9.53. $C_{69}H_{68}N_8O_9$ requires C 71.86; H 5.94; N 9.72]. Osmometric mol wt ($CHCl_3$, 37 °C) 1155 (Calc.1120.30; with 1 mol CH_3OH, 1153.30). $\lambda_{max}(\epsilon)$: 386 (9650). υ_{max}: 1452, 1275, 1209 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C): δ_H: 1.20 (12H, t, –CH_3), 1.60 (8H, q, –CH_2–Me), 2.60 (12H, s, CH_3CO), 3.60–4.30 (8H, d, AB, Ar–CH_2–Ar), 6.60–7.30 (24H, s, Ar–H).

Synthesis of 25,26,27,28-tetramethyl-p-(4-ethylphenylazo)calix[4]arene tetraketone [28] *(L2)*

To a stirred mixture of sodium iodide 4.5 g (30 mmol) and chloroacetone 2.64 ml (33.22 mmol, 3.07 g) in dry acetone (30 ml) was added, after 18 min, potassium carbonate (4.14 g, 33.60 mmol) and *p*-(4-ethylphenylazo)calix[4]arene (0.96 g, 1.01 mmol) and acetone (60 ml). The reaction mixture was heated under reflux (N_2 atmosphere) with stirring for 5 h and, after cooling, was filtered through a bed a celite, which was washed thoroughly with fresh acetone. Evaporation of the solvent furnished an orange solid that was suspended in water at 60 °C and stirred for 2 h. The product was extracted into dichlorometane, and the extract was washed with 0.1 N sodium thiosulfate and water and dried. Removal of the solvent left a dark yellow crystals solid (0.65 g), which on recrystallization from acetone furnished the tetraketone (0.56 g, 47%), mp 160 °C. [Found: C 73.77; H 6.29; N 9.35. $C_{72}H_{72}N_8O_8$ requires C 73.45; H 6.16; N 9.52]. Osmometric mol wt ($CHCl_3$, 37 °C) 1184 (Calc.1177.39). $\lambda_{max}(\epsilon)$: 384 (9600). υ_{max}: 1727, 1462, 1181 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C): δ_H: 1.20 (12H, t, –CH_3), 1.70 (8H, q, –CH_2–Me), 1.90 (12H, s, CH_3CO), 2.50 (8H, s, CH_2O–Ar), 3.60–4.10 (8H, d, AB, Ar–CH_2–Ar), 6.60–7.70 (24H, s, Ar–H).

Synthesis of 25,26,27-tribenzoyloxy-28-hydroxy-p-(4-ethylphenylazo)calix[4]arene [27] *(L3)*

A 1.90 g (1.99 mmol) sample of calix[4]arene was dissolved in 50 ml of pyridine, and 1.04 ml (8.97 mmol) of benzoylchloride was added at ice bath temperature. The mixture was stirred at 0 °C for 1 h and allowed to slowly warm to room temperature for another hour. A 300 ml portion of water was added, and the water insoluble material was collected by filtration. Recrystallization from MeOH–$CHCl_3$ afforded 1.69 g (67%) of red-brown powder, m.p. 157 °C; [Found: C 76.17; H 5.67; N 8.34. $C_{82}H_{72}N_8O_8$ requires C 75.91; H 5.59; N 8.64]. Osmometric mol wt ($CHCl_3$, 37 °C) 1307 (Calc. 1264.50; with 1 mol CH_3OH, 1297.50). $\lambda_{max}(\epsilon)$: 364 (9200). υ_{max}: 3540, 1462, 1450 cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ_H: 1.20 (12H, t, $–CH_3$), 2.63 (8H, q, $–CH_2–$Me), 3.40–4.10 (8H, d, AB, Ar–CH_2–Ar), 6.70–7.70 (39H, m, Ar–H), 8.30 (1H, s, –OH).

Synthesis of 25,26,27,28-tetraacetoxy-p-(4-n-butylphenylazo)calix[4]arene (L4)

Compound (**L4**) was prepared as described above for compound (**L1**), using acetyl chloride and obtained as a brown solid, which was filtered and washed with water and MeOH. Yield, 0.90 g (52%), m.p. 126 °C; [Found: C 73.22; H 7.07; N 8.57. $C_{77}H_{84}N_8O_9$ requires C 73.08; H 6.69; N 8.85]. Osmometric mol wt ($CHCl_3$, 37 °C) 1273 (Calc. 1272.50; with 1 mol CH_3OH, 1265.50). $\lambda_{max}(\epsilon)$: 338 (8450). υ_{max}: 1759, 1220, 1367 cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ_H: 0.80 (12H, t, $–CH_3$), 0.90–1.50 (24H, m, $–CH_2–$), 2.30 (12H, t, $CH_3–CO$), 3.10–3.90 (8H, d, AB, Ar–CH_2–Ar), 6.70–7.20 (24H, s, Ar–H).

Synthesis of 25,26,27,28-tetramethyl-p-(4-n-butylphenylazo)calix[4]arene tetraketone(L5)

Compound (**L5**) was prepared as described above for compound (**L2**), using chloro acetone and obtained as a red-brown crystals, which was filtered and washed with water and MeOH. Yield, 0.80 g (66%), m.p. 116 °C; [Found: C 74.82; H 6.76; N 8.27. $C_{80}H_{88}N_8O_8$ requires C 74.51; H 6.48; N 8.69]. Osmometric mol wt ($CHCl_3$, 37 °C) 1297 (Calc. 1289.60). $\lambda_{max}(\epsilon)$: 380 (9600). υ_{max}: 1727, 1480, 1189 cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ_H: 0.80 (12H, t, $–CH_3$), 1.00–1.60 (24H, m, $–CH_2–$), 2.20 (12H, m, CH_3CO), 2.80 (8H, t, CH_2O–Ar), 3.10–4.00 (8H, d, AB, Ar–CH_2–Ar), 6.70–7.20 (24H, s, Ar–H).

Synthesis of 25,26,27-tribenzoyloxy–28-hydroxy-p-(4-n-butylphenylazo)calix[4]arene(L6)

Compound (**L6**) was prepared as described above for compound (**L3**), using benzoyl chloride and obtained as an orange powder, which was filtered and washed with water and MeOH. Yield, 0.94 g (73%), m.p. 145 °C; [Found: C 76.98; H 6.57; N 7.63. $C_{90}H_{88}N_8O_8$ requires C 76.68; H 6.29; N 7.95]. Osmometric mol wt ($CHCl_3$, 37 °C) 1418 (Calc. 1376.70; with 1 mol CH_3OH, 1409.71). $\lambda_{max}(\epsilon)$: 320 (8000). υ_{max}: 3424, 1728, 1384, 1175 cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ_H: 0.80 (12H, t, $–CH_3$), 0.90–1.10 (24H, m, $–CH_2–$), 3.40–4.30 (8H, d, AB, Ar–CH_2–Ar), 6.90–7.40 (39H, s, Ar–H), 8.50 (1H, s, –OH).

Synthesis of 25,26,27,28-tetraacetoxy-p-(4-acetanilidazo)calix[4]arene (L7)

Compound (**L7**) was prepared as described above for compound (**L1**), using acetyl chloride and obtained as a pale brown solid, which was filtered and washed with water and MeOH. Yield, 1.14 g (56%), m.p. 142 °C; [Found: C 65.47; H 5.34; N 13.03. $C_{69}H_{64}N_{12}O_{13}$ requires C 65.29; H 5.08; N 13.24]. Osmometric mol wt ($CHCl_3$, 37 °C) 1277 (Calc. 1236.30; with 1 mol CH_3OH, 1269.30). $\lambda_{max}(\epsilon)$: 352 (8800). υ_{max}: 1739, 1480, 1221 cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ_H: 0.80 (12H, t, $–CH_3$), 2.30 (12H, s, CH_3CO), 3.20–3.70 (8H, d, AB, Ar–CH_2–Ar), 6.5 (4H, s, –NH–), 7.20–7.70 (24H, s, Ar–H).

Synthesis of 25,26,27,28−tetramethyl-p-(4-acetanilidazo)calix[4]arene tetraketone (L8)

Compound (**L8**) was prepared as described above for compound (**L2**), using chloro acetone and obtained as pale brown crystals solid, which was filtered and washed with water and MeOH. Yield, 1.23 g (51%), m.p. 138 °C; [Found: C 67.02; H 5.57; N 12.63. $C_{72}H_{68}N_{12}O_{12}$ requires C 66.86; H 5.30; N 13.00]. Osmometric mol wt ($CHCl_3$, 37 °C) 1307 (Calc. 1293.38). $\lambda_{max}(\epsilon)$: 356 (8900). υ_{max}: 1728, 1482, 1200 cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ_H: 0.80 (12H, t, $–CH_3$), 1.90 (12H, s, CH_3CO), 3.30 (8H, s, $–CH_2–O$), 3.80–4.30 (8H, d, AB, Ar–CH_2–Ar), 6.40 (4H, s, –NH–), 7.10–7.40 (24H, s, Ar–H).

Synthesis of 25,26,27-tribenzoyloxy-28-hydroxy-p-(4-acetanilidazo)calix[4]arene (L9)

Compound (**L9**) was prepared as described above for compound (**L3**), using benzoyl chloride and obtained as a dark orange solid, which was filtered and washed with water and MeOH. Yield, 0.93 g (72%), m.p. 153 °C; [Found: C 69.70; H 4.78; N 11.89. $C_{82}H_{68}N_{12}O_{12}$ requires C 63.67; H 4.84; N 11.89]. Osmometric mol wt ($CHCl_3$, 37 °C) 1428 (Calc. 1380.50; with 1 mol CH_3OH, 1413.49). $\lambda_{max}(\epsilon)$: 364 (9200). υ_{max}: 3536, 1733, 1451, 1264 cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ_H: 1.30 (12H, s, CH_3CO), 3.40–4.10 (8H, d, AB, Ar–CH_2–Ar), 6.60 (4H, s, NH), 7.20–7.70 (39H, s, Ar–H), 8.60 (1H, s, –OH).

Synthesis of 25,26,27,28-tetraacetoxy-p-(2-thiazolazo)calix[4]arene (L10)

Compound (**L10**) was prepared as described above for compound (**L1**), using acetyl chloride and obtained as a pale brown powder, which was filtered and washed with

water and MeOH. Yield, 1.07 g (51%), m.p. 140 °C; [Found: C 55.72; H 3.93; N 15.50; S 11.90. $C_{49}H_{40}N_{12}S_4O_9$ requires C 55.04; H 3.77; N 15.72; S 12.00]. Osmometric mol wt ($CHCl_3$, 37 °C) 1083 (Calc. 1036.20; with 1 mol CH_3OH, 1069.20). $\lambda_{max}(\epsilon)$: 366 (9150). υ_{max}: 1758, 1481, 1219 cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ_H: 2.10 (12H, s, CH_3CO), 3.20–4.20 (8H, d, AB, Ar–CH_2–Ar), 6.80–7.20 (8H, s, Ar–H), 7.41–7.87 (8H, 2d, =CH).

Synthesis of 25,26,27,28-tetra methyl-p-(2-thiazolazo) calix[4]arene tetraketone (L11)

Compound (**L11**) was prepared as described above for compound (**L2**), using chloro acetone and obtained as a red crystals, which was filtered and washed with water and MeOH yield, 1.33 g (62%), m.p. 118 °C; [Found: C 57.34; H 4.23; N 15.07; S 11.48. $C_{52}H_{44}N_{12}S_4O_9$ requires C 57.13; H 4.06; N 15.38; S 11.73]. Osmometric mol wt ($CHCl_3$, 37 °C) 1102 (Calc. 1093.25). $\lambda_{max}(\epsilon)$: 364 (9100). υ_{max}: 1732, 1480, 1188, cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ_H: 2.90 (12H, s, CH_3CO), 3.30 (8H, s, –CH_2–O), 3.40–4.40 (8H, d, AB, Ar–CH_2–Ar), 6.80–7.20 (8H, s, Ar–H), 7.52–7.91 (8H, 2d, =CH).

Synthesis of 25,26,27-tribenzoyloxy-28-hydroxy-p-(2-thiazolazo)calix[4]arene (L12)

Compound (**L12**) was prepared as described above for compound (**L3**), using benzoyl chloride and obtained as an orange powder, which was filtered and washed with water and MeOH. Yield, 1.05 g (75%), m.p. 147 °C; [Found: C 61.54; H 3.86; N 13.61; S 10.34. $C_{62}H_{44}N_{12}S_4O_8$ requires C 61.37; H 3.65; N 13.85; S 10.57]. $\lambda_{max}(\epsilon)$: 272 (6800). υ_{max}: 3173, 1482, 1219 cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ_H: 3.40–4.20 (8H, d, AB, Ar–CH_2–Ar), 7.00–7.20 (23H, m, Ar–H), 10.20 (1H, s, –OH), 7.45–7.92 (8H, 2d, =CH).

References

1. C.D. Gutsche: In J.F. Stoddart (ed.), *In Calixarenes Revisited: Monographs in Supramolecular Chemistry*, The Royal Society of Chemistry, London (1998), pp. 149–167.
2. M. Liebau, J. Huskens, and D.N. Reinhoudt: *Adv. Funct. Mater.* **2**, 147 (2001).
3. W.F. Nijenhuis, E.G. Buitenhuis, F. De Jong, E.J.R. Sudhölter, and D.N. Reinhoudt: *J. Am. Chem. Soc.* **113**, 7963 (1991).
4. H.-G. Löhr and F. Vögtle: *Acc. Chem. Res.* **18**, 65 (1985).
5. J. Vicens and V. Böhmer: *Calixarenes*: A versatile Class of Macrocyclic Compounds, Kluwer (1991).
6. F. Vögtle, D. Udelhofen, S. Abramson, and B. Fuchs: *J. Photochem. Photobiol. A., Chem.* **131**, 41 (2000).
7. S. Bouoit-Montesinos, J. Bassus, M. Perrin, and R. Lamartine: *Tetrahedron Lett.* **41**, 2563 (2000).
8. M. Saadioui, Z. Asfari, J. Vicens, N. Reynier, and J.-F. Dozol: *J. Incl. Phenom.* **28**, 223 (1997).
9. A. Akdoğan, M. Deniz (Tavaslı), S. Cebecioğlu, A. Sen, and H. Deligöz: *Sep. Sci. Technol.* **37**, 973 (2002).
10. R. Ludwig: *Fresenius J. Anal. Chem.* **367**, 103 (2000).
11. G. Uysal, S. Memon, and M. Yılmaz: *React. Funct. Polym.* **50**, 77 (2001).
12. H. Shimuzu, K. Iwamato, K. Fujimoto, and S. Shinkai: *Chem. Lett.* 2147 (1991).
13. Y. Morita, T. Agawa, Y. Nomura, and H. Taniguchi: *J. Org. Chem.* **57**, 3658 (1992).
14. S. Shinkai, K. Araki, J. Shibata, D. Tsugawa, and O. Manabe: *J. Chem. Soc., Perkin Trans.* **1, 1990**, 3333–3337.
15. H. Deligöz and M. Yilmaz: *Synth. React. Inorg. Met. -Org. Chem.* **26**, 943 (1996).
16. H. Deligöz: *J. Incl. Phenom.* **39**, 123 (2001).
17. H. Deligöz, A.İ. M.A. Pekacar Özler, and M. Ersöz: *Sep. Sci. Technol.* **34**, 3297 (1999).
18. H. Deligöz, H.K. Alpoğuz, and H. Çetisli: *J.M.S., -Pure Appl. Chem.* **37**, 407 (2000).
19. H. Deligöz, M. Tavaslı, and M. Yilmaz: *J. Polym. Sci. Pol. Chem.* **32**, 2961 (1994).
20. H. Deligöz and M. Yilmaz: *J. Pol. Sci. Pol. Chem.* **33**, 2851 (1995).
21. M. Yilmaz and H. Deligöz: *Sep. Sci. Technol.* **31**, 2395 (1996).
22. S. Memon, G. Uysal, and M. Yilmaz: *Sep. Sci. Technol.* **35**, 1247 (2000).
23. H. Deligöz and N. Ercan: *Tetrahedron* **58**, 2881 (2002).
24. H. Deligöz and H. Çetisli: *J. Chem. Res.* **10**, 427 (2001).
25. C.D. Gutsche and M. Iqbal: *Org. Synth.* **68**, 234 (1990).
26. C.D. Gutsche, M. Iqbal, and D. Stewart: *J. Org. Chem.* **51**, 742 (1986).
27. C.D. Gutsche and L.G. Lin: *Tetrahedron* **42**, 1633 (1986).
28. F. Arnaud-Neu, E.M. Collins, M. G. Deasy Ferguson, S.J. Harris, B. Kaitner, A.J. Lough, M.A. Mckervey, E. Marques, B.L. Ruhl, M.J. Schwing-Weill, and E.M. Seward: *J. Am. Chem. Soc.* **111**, 8681 (1989).