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Azocalixarenes. 2: synthesis, characterization and investigation of the absorption spectra of azocalix[6]arenes containing chromogenic groups

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Abstract

Twelve new azocalix[6]arenes (**1–12**) have been synthesized by linking *o*-, *m*-, *p*-chloroaniline, *o*-, *m*-, *p*-nitroaniline, *o*-, *m*-, *p*-toluidine, *m*-, *p*-anisidine and aniline to calix[6]arene through a diazo-coupling reaction. The prepared compounds were characterized based on UV–vis, FT–IR and ^{1}H-NMR spectroscopic techniques as well as elemental analysis. The effect of varying pH and solvent upon the absorption ability of azocalixarenes substituted with electron-donating and electron-withdrawing groups at their *o*-, *m*-, *p*-position was examined. Observed results were compared with those found for unsubstituted azocalix[6]arenes. Concentration effects on the visible absorption maxima of the dyes are also reported.

Keywords: Calixarene; Azocalix[6]arenes; Calixarene dyes; Diazo-coupling reaction; Solvent effect; Substituent effect; Absorption spectra

1. Introduction

Calix[*n*]arenes represent macrocyclic compounds widely used in supramolecular chemistry for the construction of various receptors for the complexation of charged or neutral molecules [1]. Their unique three-dimensional structures with almost unlimited derivatization abilities and a tuneable shape of the molecules make calixarenes ideal candidates for building blocks and/or molecular scaffolds in the design of new more sophisticated molecules. Calixarenes have several attractive features as macrocycles of higher degree of preorganization. They are formed by *para*-phenolic units linked by methylene bridges *ortho* to the OH functions. Calixarene can be chemically modified by substitution of the phenolic hydrogens with various types of functions known for their affinity of the cation of interest [2]. Furthermore, phenolic groups can be functionalized on the *para* position to make the calixarene either lipophobic or lipophilic.

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The construction of ion selective molecular sensors continues to attract attention due to potential applications and as a testing ground for molecular recognition and signal transduction schemes. Progress in the field, has been reviewed in recent years [3,4]. In conjugated donor–acceptor chromophores or fluorophores (internal change transfer-ICT sensors), if the receptor is a part of the donor moiety, cation binding induces a blue-schift (hypsochromic effect) with a decrease in the extinction coefficient (anti-auxochromic effect): however, if the acceptor, group is part of the receptor then there is a red-shift (bathochromic effect) with an increase in extinction coefficient results (auxo-chromic effect) on cation binding [5].

It has been known for many years that the azo compounds are the most widely used class of dyes due to their versatile application in various fields such as the dyeing of textile fiber, the coloring of different materials, coloured plastics, biological-medical studies and advanced applications in organic synthesis. Many patents and papers describe the synthesis and dyeing properties of azo compounds [6–9].

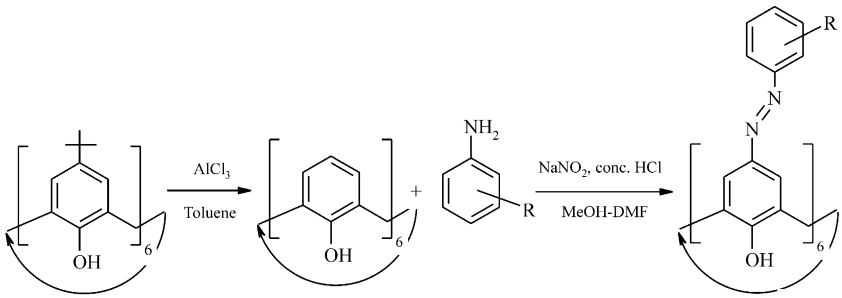
In our recent work, we have synthesized the most various derivatives of calix[*n*]arene [10–13] and their complexes [14], polymeric calix[*n*]arene derivatives [15] and liquid–liquid [16] or selective [17] extraction of transition metal cations.

In this study the calixarene is composed of a ring of six phenolic units used as molecular substructures, on which preorganized ligands, such as the six azo groups in C_6 symmetry are assembled to provide the required structure (Scheme 1). In this paper, the application of amphiphilic calix[6]arenes (**1–12**) are reported for the effect of varying pH and solvent upon the absorption ability of azocalixarenes substituted with electron-donating and electron-withdrawing groups at their *o*-, *m*-, *p*- position.

2. Experimental

2.1. General

All solvents and commercial grade reagents used were purchased from Merck or Carlo-Erba and were chemically pure. Melting points were determined using an Electrothermal IA9100 digital melting point apparatus and are uncorrected. ^{1}H NMR spectra were referenced to tetramethylsilane (TMS) at 0.00 ppm as internal standard and were recorded on a Bruker 400 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 160A UV–Visible recording spectrophotometer. Solvent of crystallization was retained in some of the



(1) : R= *o*-Cl
(2) : R= *m*-Cl
(3) : R= *p*-Cl
(4) : R= *o*-NO_2
(5) : R= *m*-NO_2
(6) : R= *p*-NO_2
(7) : R= *o*-CH_3
(8) : R= *m*-CH_3
(9) : R= *p*-CH_3
(10): R= *m*-OCH_3
(11): R= *p*-OCH_3
(12): R= H

Scheme 1. *o*-, *m*-, *p*-Substituted azocalix[6]arene derivatives.

analytical samples of affected the elemental analysis. In such cases, best first between the analytical values and appropriate fractional increments of solvents were used. Osmometric molecular mass determinations were carried out on a Knauer vapor pressure osmometer at concentrations of ca. 10^{-3} mol/L in DMSO. The elemental analyses were performed in the TUBITAK Laboratory (Center of Science and Technology Research of Turkey).

2.2. Preparation of the ligands

p-tert-Butylcalix[6]arene [18] and calix[6]arene [19] were synthesized as described by a previously reported method.

2.3. Synthesis of phenylazocalix[6]arene (*1–12*)

Diazotisation of the various carbocyclic amines was effected with HCl. A typical procedure is that described below used for 2-chloroaniline. *p*-(3-Chlorophenylazo)calix[6]arene (**2**), *p*-(4-chlorophenylazo)calix[6] arene (**3**), *p*-(2-nitrophenylazo)-calix[6]arene (**4**), *p*-(3-nitrophenylazo)calix[6]arene (**5**), *p*-(4-nitrophenylazo)calix[6]arene (**6**), *p*-(2-methylphenylazo)calix[6]arene (**7**), *p*-(3-methylphenylazo)calix[6]arene (**8**), *p*-(4-methylphenylazo)-calix[6]arene (**9**), *p*-(3-metoxyphenylazo)calix[6]arene (**10**), *p*-(4-methoxyphenylazo)calix[6]arene (**11**) and *p*-(phenylazo)calix[6]arene (**12**) were obtained using the same method in 64–90% yield. The obtained compounds were purified by crystallization using the same solvent (DMF–H_2O) and were then analyzed. Characterisation data are shown in Tables 1 and 2.

2.3.1. The synthesis of p-(2-chlorophenylazo)-calix[6]arene (*1*)

A solution of 2-chlorophenyldiazonium chloride, which was prepared from 2-chloroaniline

Table 1
Spectral data for dyes **1–12**

Dye no.	IR (cm^{-1}) in KBr						^{1}H-NMR (δ, ppm)			
	ν_{O-H}	$\nu_{C-H(aro.)}$	$\nu_{C-H(alip.)}$	$\nu_{C=C}$	$\nu_{N=N}$	ν_{C-O}	Aro-H	Alip-H	X-H	Solvent
1	3223	3089 3036	2946	1679	1598	1100	6.81–8.23 (36H, m)	2.18 and 4.23 (12H,s)	10.95 (OH, b) 13.87 (NH, b)	DMSO-d_6
2	3250	3107 3036	2929	1696	1611	1089	6.78–8.00 (36H, m)	2.12 and 4.15 (12H, s)	10.82 (OH, b) 13.95 (NH, b)	DMSO-d_6
3	3223	3107 3045	2955	1714	1625	1107	7.22–7.86 (36H, m)	2.24 and 4.17 (12H, s)	10.90 (OH, b) 13.75 (NH, b)	DMSO-d_6
4	3223	3086 3018	2929	1679	1608	1071	7.02–8.05 (36H, m)	2.24 and 4.17 (12H, s)	11.43 (OH, b) 14.37 (NH, b)	DMSO-d_6
5	3271	3107 3036	2955	1696	1592	1107	7.19–8.35 (36H, m)	2.18 and 4.21 (12H, s)	11.51 (OH, b) 14.28 (NH, b)	DMSO-d_6
6	3268	3098 3054	2946	1685	1589	1083	7.13–8.11 (36H, m)	2.15 and 4.18 (12H, s)	11.47 (OH, b) 14.38 (NH, b)	DMSO-d_6
7	3250	3089 3036	2946	1679	1598	1075	7.06–7.79 (36H, m)	2.20 and 4.25 (12H, s) 2.09 and 2.71 (18H, s)	12.25 (OH, b) 14.65 (NH, b)	DMSO-d_6
8	3232	3086 3018	2938	1675	1591	1089	6.70–7.88 (36H, m)	2.15 and 4.20 (12H, s) 2.24 (18H, s)	12.30 (OH, b) 14.75 (NH, b)	DMSO-d_6
9	3223	3089	2964	1679	1593	1089	7.00–7.84 (36H, m)	2.20 and 4.25 (12H, s) 2.17 and 2.39 (18H, s)	11.85 (OH, b) 14.15 (NH, b)	DMSO-d_6
10	3200	3089	2950	1682	1607	1116	6.42–7.71 (36H, m)	2.18 and 4.20 (12H, s) 3.71 (18H, s)	11.70 (OH, b) 14.10 (NH, b)	DMSO-d_6
11	3214	3089 3054	2948	1679	1616	1143	6.80–7.78 (36H, m)	2.17 and 4.23 (12H, s) 3.65 (18H, s)	11.80 (OH, b) 14.17 (NH, b)	DMSO-d_6
12	3205	3085 3030	2946	1652	1580	1150	7.01–8.03 (42H, m)	2.24 and 4.13 (12H,s)	11.97 (OH, b) 14.28 (NH, b)	DMSO-d_6

X: O, N, s: singlet, m: multiplet, b: broad.

Table 2
Element analysis of dyes **1**–**12**

Dye no.	Molecular formula	Molecular mass	Yield %	C %		H %		N %		Melting point °C
				Calcd.	Found	Calcd.	Found	Calcd.	Found	
1	$C_{78}H_{54}Cl_6N_{12}O_6$	1467	87	63.82	64.42	3.71	4.01	11.45	11.12	dec.300
2	$C_{78}H_{54}Cl_6N_{12}O_6$	1467	80	63.82	64.46	3.71	4.11	11.45	11.08	dec.300
3	$C_{78}H_{54}Cl_6N_{12}O_6$	1467	83	63.82	64.35	3.71	3.95	11.45	10.97	dec.300
4	$C_{78}H_{54}N_{18}O_{18}$	1530	81	61.18	61.13	3.55	3.81	16.46	15.95	dec.290
5	$C_{78}H_{54}N_{18}O_{18}$	1530	90	61.18	61.38	3.55	3.78	16.46	15.91	dec.300
6	$C_{78}H_{54}N_{18}O_{18}$	1530	80	61.18	61.67	3.55	3.73	16.46	16.05	dec.285
7	$C_{84}H_{72}N_{12}O_6$	1344	69	74.98	75.38	5.39	5.52	12.49	11.96	dec.295
8	$C_{84}H_{72}N_{12}O_6$	1344	64	74.98	75.63	5.39	5.48	12.49	12.13	dec.280
9	$C_{84}H_{72}N_{12}O_6$	1344	78	74.98	75.55	5.39	5.61	12.49	11.98	dec.280
10	$C_{84}H_{72}N_{12}O_{12}$	1440	84	69.99	70.51	5.03	5.28	11.66	11.24	dec.280
11	$C_{84}H_{72}N_{12}O_{12}$	1440	86	69.99	70.47	5.03	5.25	11.66	11.29	dec.300
12	$C_{78}H_{60}N_{12}O_6$	1260	80	74.27	74.66	4.79	4.92	13.32	12.93	dec.290

(2.54 g, 20 mmol), sodium nitrite (1.38 g, 20 mmol) and conc. HCl (15 mL) in water (40 mL), was added slowly to a cold (5 °C) solution of calix[6]arene (1.50 g, 2.36 mmol) and sodium acetate trihydrate (8.16 g, 60 mmol) in MeOH–DMF (52 mL, 5:8, v/v) to give a light orange suspension. After standing for 2 h at room temperature, the suspension was acidified with aqueous HCl (300 mL, 0.25%) and the mixture was then warmed to 60 °C for 30 min to give **1** (yield, 3.12 g, 90%) as a light orange solid, which was filtered and washed with water and MeOH. **1** was dissolved in 100 mL of hot aqueous $NaHCO_3$ (4.2 g) solution; to this solution was added activated charcoal (1 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 to 60 °C again for 30 min and then cooled. The resulting solid was filtered, washed with water, and dried. Recrystallization from DMF–H_2O mixture gave a light orange solid [yield, 3.0 g (87%), m.p. dec. > 300 °C].

3. Results and discussion

3.1. Synthesis and characterizations

In the present investigation, some new *o*-, *m*-, *p*-substituted (–Cl, $–NO_2$, $–CH_3$, and $–OCH_3$) aniline derivatives were prepared. The effect of the nature of substituents on the colour of the azocalix[6]-arenes is discussed. Their dyeing behaviour and performance on solvent and substituent effects were assessed.

In order to explore azocalixarene chemistry further and to continue our previous work in this area, the synthesis of some azocalix[4]arene derivatives are reported. No details of the synthesis and wave-length shift behaviour of such compounds have been published hitherto.

In a search for some new azocalix[6]arenes (**1**–**12**), the present investigation was focused on the diazo-coupled calix[6]arene with some *o*-, *m*-, *p*-substituted aniline derivatives in the present of sodium nitrite/conc. HCl. Similarly, the same products were obtained when the diazo-coupled reaction was carried out in the presence of MeOH–DMF and freshly fused sodium acetate.

In this work, we report the synthesis of 12 new azocalix[6]arenes moieties (upper rim connected by six *o*-, *m*-, *p*-diazonium salt derivatives linkage). At first *p-tert*-butylcalix[6]arene was prepared by reaction of *p-tert*-butylphenol with formaldehyde according to the method of Gutsche [18]. Treatment of *p-tert*-butylcalix[6]arene with aluminium chloride gave calix[6]arene according to the method described by Gutsche et al. [19]. Then we synthesized the diazonium salt derivatives described herein were synthesized according to the method

described by Morita et al. [20], after then we employed 8 equivalent of these salts in 5:8 MeOH–DMF mixture with 1 equivalent of calix[6]arene to obtain the corresponding azocalix[6]arenes **1**–**12**. The general reaction described in Scheme 1.

The diazonium salts were excellent electrophiles and would attack any available position on the calix[*n*]arenes to yield a complex mixture. Work up of the reaction mixtures afforded the corresponding six azophenylcalix[6]arenes in 64–90% yields.

The above reaction products were characterized by elemental analysis, FT-IR and ^{1}H-NMR spectral data. ν_{max} values of 3271–3200 cm^{-1} (OH), 3107–3086 and 3056–3018 cm^{-1} (aromatic C–H), 2955–2929 cm^{-1} (aliphatic C–H), 1714–1652 cm^{-1} (C=C), 1625–1580cm^{-1} (N=N) and 1150–1089 cm^{-1} (C–O) were recorded. The ^{1}H-NMR spectrum of **1**–**12** revealed a singlet peak for methylene protons (–CH_2–) at δ 2.12–2.24 and 4.13–4.25, a singlet at 2.09–2.24 and 2.39–2.71 (–CH_3), a singlet at 3.65–3.71 (–OCH_3), a multiplet from 6.70–8.35 for aromatic protons (Aro-H), a broad peak at 10.82–12.30 (OH) and a broad peak at 13.75–14.75 (NH).

Such a diazo-coupling reaction between calix[6]arene and aniline derivatives was eventually achieved by cooling the reaction mixture at 0 °C in the presence of freshly fused sodium acetate for 2 h to give the corresponding *o*-, *m*-, *p*-substituted aniline derivatives. Since the compounds obtained (**1**–**12**) varied in colour from brown to yellow, a convenient method of measuring the colour of these compounds was to study the absorption spectra of their solutions.

Conformational study has been realized by ^{1}H-NMR spectra at room temperature. Thus, at 25 °C hydroxy and imine ($\delta = 10.82$–12.30 and 13.75–14.75) protons display two broad singlets for **1**–**12**. At room temperature the singlets indicate that the calixarenes are conformationally mobile. In the case of azocalix[6]arene the phenomenon is the same, but at room temperature, there is only one broad singlet showing a better mobility then in azocalix[4]arene. Indeed, in an azocalix[6]arene mobility is more easy then in azocalix[4]arene in relation with difference of size and a less strong hydrogen bond stabilization.

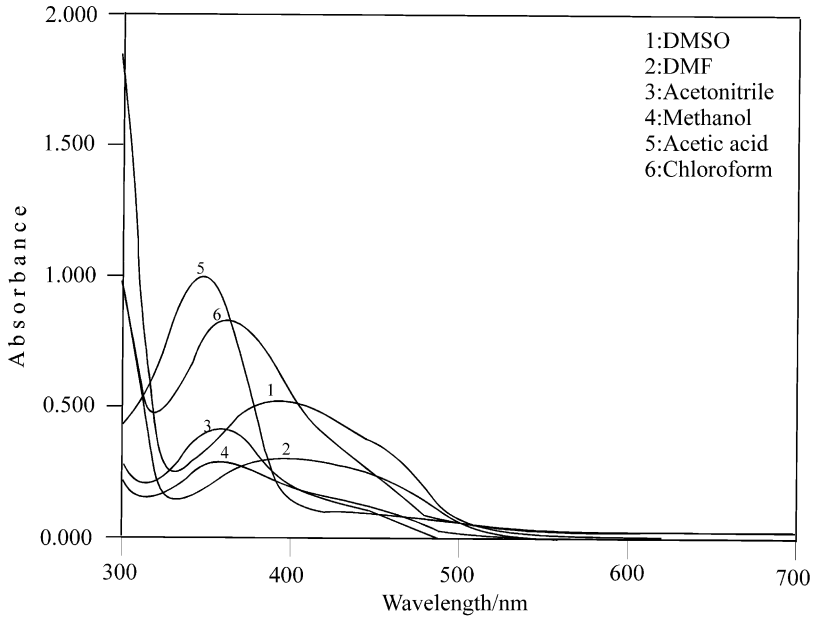


Fig. 1. Absorption spectra of dye **9** in various solvents.

Table 3
Influence of solvent on λ_{max} (nm) of dyes **1–12**

Dye no.	DMSO		DMF		Acetonitrile		Methanol		Acetic acid		Chloroform	
	Conc.	Dil.	Conc.	Dil.	Conc.	Dil.	Conc.	Dil.	Conc.	Dil.	Conc.	Dil.
1	404, 460 s, 552 s	407, 463 s, 554 s	408, 461 s, 552 s	408, 460 s, 553 s	380	381	393	391	359, 449 s	359, 450 s	369, 455 s	369, 453 s
2	423, 456 s, 551 s	423, 455 s, 553 s	420, 455 s, 550 s	420, 456 s, 551 s	388	389	381	396	362, 440 s	362, 440 s	369, 443 s	368, 443 s
3	433, 396 s	433, 395 s	428, 390 s	429, 392 s	356, 428 s	358, 430 s	365, 432 s	364, 432 s	352, 433 s	352, 433 s	358, 430 s	356, 427 s
4	392, 482 s	393, 483 s	392, 481 s	392, 480 s	391, 344 s	389, 343 s	391	390	387, 346 s, 480 s	386, 346 s, 481 s	393, 342 s	392, 340 s
5	312, 329 s, 461 s	312, 328 s, 461 s	310, 327 s, 460 s	308, 325 s, 458 s	326, 405 s	326, 404 s	324, 405 s	325, 406 s	334, 461 s	334, 461 s	330, 403 s	329, 403 s
6	412, 520 s	414, 523 s	408, 512 s	408, 508 s	393, 468 s	393, 468 s	397, 470 s	397, 470 s	390, 463 s	391, 465 s	392, 469 s	392, 468 s
7	365, 432 s	365, 432 s	363, 430 s	363, 430 s	354, 429 s	354, 429 s	356, 430 s	357, 430 s	353, 428 s	353, 427 s	356, 430 s	354, 428 s
8	367, 435 s	366, 435 s	364, 432 s	364, 433 s	353, 428 s	352, 428 s	357, 430 s	357, 430 s	352, 429 s	352, 428 s	354, 430 s	355, 430 s
9	391, 463 s	390, 446 s	398, 449 s	400, 450 s	356, 430 s	358, 431 s	368, 432 s	367, 432 s	349, 427 s	349, 428 s	362, 433 s	362, 434 s
10	391, 463 s	391, 464 s	390, 462 s	389, 462 s	371, 442 s	371, 441 s	371, 440 s	375, 442 s	357, 439 s	357, 438 s	369, 440 s	369, 441 s
11	387, 460 s	385, 459 s	383, 458 s	387, 461 s	362, 437 s	363, 439 s	361, 438 s	362, 438 s	362, 438 s	357, 435 s	362, 438 s	362, 438 s
12	430	431	367, 430 s	364, 428 s	353, 410 s	352, 409 s	371, 427 s	371, 427 s	347, 410 s	346, 409 s	349, 411 s	348, 411 s

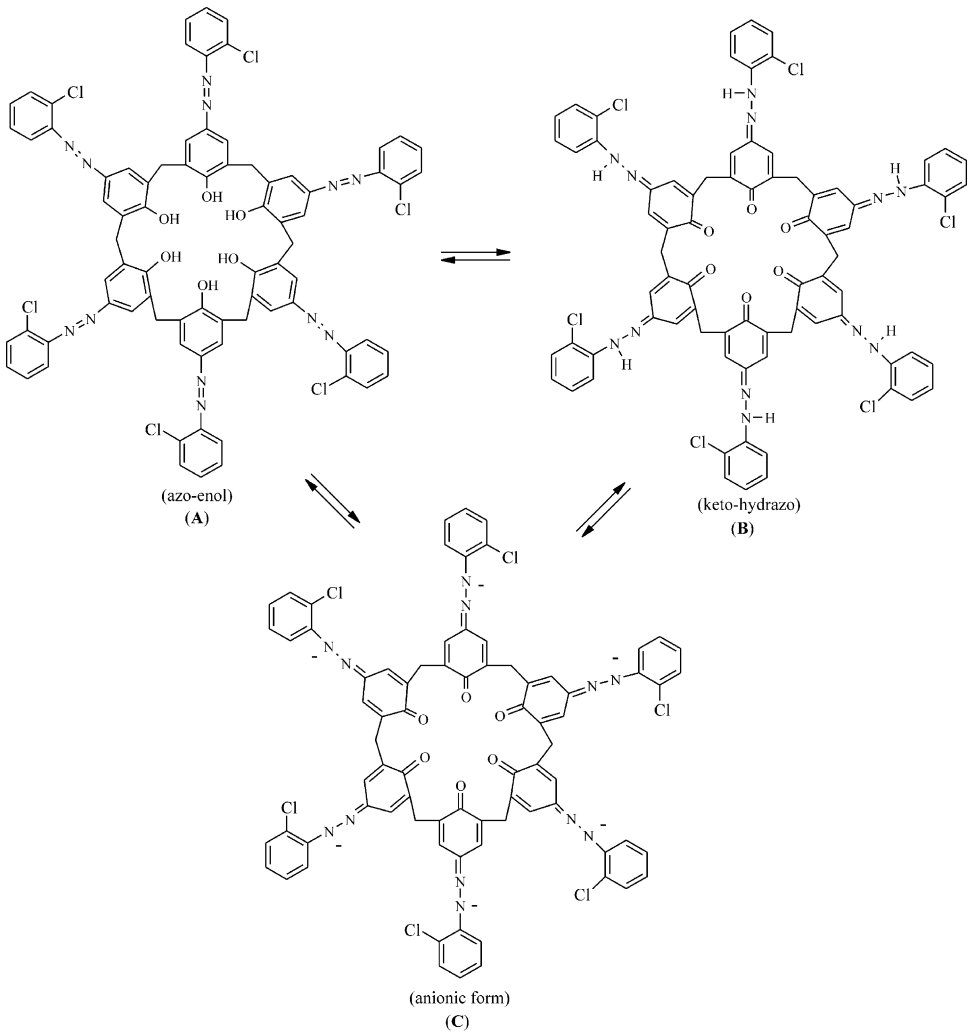
s: shoulder, conc.: concentrated, dil.: diluted.

The present paper describe for the first time the synthesis of calix[6]arenes both azo-enol form and keto-hydrazo form bearing both azo and substitue groups. Application to these new compounds in field of absorption spectra and variety solvent or pH change have been investigated.

3.2. Solvent effect

UV–vis absorption spectra were measured using a Shimadzu 160A spectrophotometer in the wavelength range 300–700 nm. Absorption spectra of azocalixarenes were measured various solvents and pH. The pH value of all solutions used was in the range between acidic and basic. The choice of solvent is based on their polarity. The work is mainly concerned with the shift effect of solubility and pH. Effect of substituents have also been considered. More detailed analysis of the effects of various solvents and pH change has been performed in relation to azocalixarene **9** solutions only.

Typical absorption spectra of azocalix[6]arene **9** is shown in different solvents in Fig. 1. The main absorption band around 385 nm corresponds to the π–π* transition of azo-chromophore in azo-



Scheme 2. The tautomeric forms and anionic form of 4-(2-chlorophenylazo)calix[6]arene (**1**).

enol form. It can be seen that the position of the absorption maximum is slightly shifted to the high wavelength side (red shift) as compared with the peak position in the solution spectrum at 375 nm, which usually corresponds to isolated molecules. This shift can simply be explained by conjugation of substitue azo derivatives in calixarene structure.

Effect of various pH and solution concentration on the absorption intensity have been studied in more details. The absorption spectra of azocalix[6]arene **1**–**12** were recorded in various solvents at a concentration of $\sim 10^{-6}$–$\sim 10^{-8}$ M; the recorded results are summarized in Table 3. The spectra of azocalix[6]arenes were found to exhibit strong solvent dependency, which did not show regular variation with the polarity of solvents.

It was observed that the absorption spectra of the compounds in all solvents generally change with respect to the absorption spectra in chloroform. The λ_{max} of the compounds shifted considerably in DMF and DMSO (e.g. for compound **3** λ_{max} is 358 nm in $CHCl_3$, 428 nm in DMF and 433 nm in DMSO; for compound **6** is 392 nm in $CHCl_3$, 408 nm in DMF and 412 nm in DMSO; for compound **11** is 362 nm in $CHCl_3$, 383 nm in DMF and 387 nm in DMSO).

Strong evidence for the existence of these compounds existing in an equilibrium is provided by the isosbestic points in the visible spectra of for example compound **9** in different solvents (Fig. 1). This equilibrium may exist between tautomeric forms. But, compounds **1**, **2** and **5** showed three absorption peaks in DMF and DMSO. The equilibrium of compounds **1**, **2** and **5** in DMF and DMSO may exist between tautomeric forms and anionic form. Absorption peaks at the longest wavelegth of compounds **1**, **2** and **5** may a peak of anionic form. This indicates that the compounds **1**, **2** and **5** exist in a dissociated state in DMF and DMSO (Scheme 2).

The equilibrium depends on the basidity of the solvents used; in proton accepting solvents such as DMSO, DMF, acetonitrile, methanol, the compounds displayed a red shift of the λ_{max}. In a proton donating solvent such as acetic acid, the λ_{max} of the compounds displayed slightly a blue shift of the λ_{max} respect to the absorption spectra in chloroform with the exception of compound **5**.

Table 4
Absorption maxima (nm) of dyes **1**–**12** in acidic and basic solutions

Dye no.	Chloroform	Chloroform + piperidine	Acetic acid	Methanol	Methanol + KOH	Methanol + HCl	DMSO	DMSO + piperidine	DMF	DMF + piperidine
1	369, 453 s	391, 550 s	359, 450 s	391	396	387	407, 463 s, 554s	427, 471 s, 600 s	408, 460 s, 553 s	408, 460 s, 553 s
2	368, 443 s	391, 455 s, 548 s	362, 440 s	396	401	378	423, 455 s, 553 s	426, 457s, 558 s	408, 460 s, 553 s	421, 455 s, 550 s
3	356, 427 s	391, 429 s	352, 433 s	364, 432 s	405, 440 s	355, 432 s	433, 395 s	456, 415 s	429, 392 s	459, 417 s
4	392, 340 s	392, 481 s	386, 346 s, 481 s	390	391, 484 s	385	393, 483 s	394, 484 s	392, 480 s	393, 482 s
5	329, 403 s	328, 405 s	334, 461 s	325, 406 s	329, 406 s	325, 406 s	312, 328 s, 461 s	403, 478 s	308, 325 s, 458 s	401, 475 s
6	392, 468 s	405, 483 s	391, 465 s	397, 470 s	518, 391 s	397, 469 s	414, 523 s	578, 424 s	408, 508 s	579, 427 s
7	354, 428 s	365, 432 s	353, 427 s	357, 430 s	405, 451 s	357, 430 s	365, 432 s	367, 435 s, 482 s	363, 430 s	363, 430 s, 452 s
8	355, 430 s	362, 432 s	352, 428 s	357, 430 s	409, 430 s	354, 428 s	366, 435 s	482, 376 s, 436 s	364, 433 s	366, 480 s
9	362, 434 s	389, 447 s	349, 428 s	367, 432 s	385, 448 s	351, 427 s	390, 446 s	423, 461 s	400, 450 s	420, 460 s
10	369, 441 s	389, 462 s	357, 438 s	375, 442 s	410, 448 s	368, 435 s	391, 464 s	467, 436 s, 576 s	389, 462 s	424, 456 s, 570 s
11	362, 438 s	389, 461 s	357, 435 s	362, 438 s	392, 465 s	359, 432 s	385, 459 s	423, 476 s	387, 461 s	421, 474 s
12	348, 411 s	395, 428 s	346, 409 s	371, 427 s	394, 425 s	351, 410 s	431	430	364, 428 s	433

s: shoulder.

The λ_{max} of the compounds showed bathochromic effects when a small amount of piperidine was added to each of the compound solutions in chloroform, DMSO or DMF (Table 4); a typical example is shown in Fig. 2. The λ_{max} of the compounds in methanol also showed bathochromic effects when 0.1M KOH was added. These findings indicates that compounds **1**–**12** exist in the anionic form in chloroform + piperidine, DMSO + piperidine, DMF + piperidine and methanol + KOH. The λ_{max} of the compounds in methanol also showed slightly hypsochromic effects when 0.1M HCl was added (Table 4).

The effect of concentration of the compound on absorption maxima was examined (Table 3). The λ_{max} of all compounds did not change with compound concentration.

3.3. Substituent effects

The UV spectra of compounds **1**–**12** in chloroform showed two bands in the region 300–700 nm. The relatively small difference in the λ_{max} may be caused by the polarity change of the absorbing system caused by solvent interactions due to the general solvent effect.

It has been reported that the UV spectra of the azocalixarenes generally show two absorption bands at 400–570 nm (shoulder) and 300–400 nm corresponding to n–π* and π–π* transitions respectively.

It is clear that the band at the longer wavelength seem to be modified by polar substituents in the arylazo moiety, whereas the shorten wavelength band is uneffected. Table 3 shows that both electron-donating and electron-withdrawing groups cause the absorption spectra to the higher wavelengths.

Table 3 also shows that the presence of electron-donating or electron-withdrawing groups has not brought about any marked increase or decrease in the λ_{max} in the visible 300–600 nm.

Generally, variation in colour of the azocalix[6]-arenes **1**–**12** depends on substitution in the substitute aniline derivatives and calix[6]arene components. Within the series of azocalixarenes investigated, the relationship between the shift observed in the absorption maxima, and polar characteristics of substituent, may be summarized as follows:

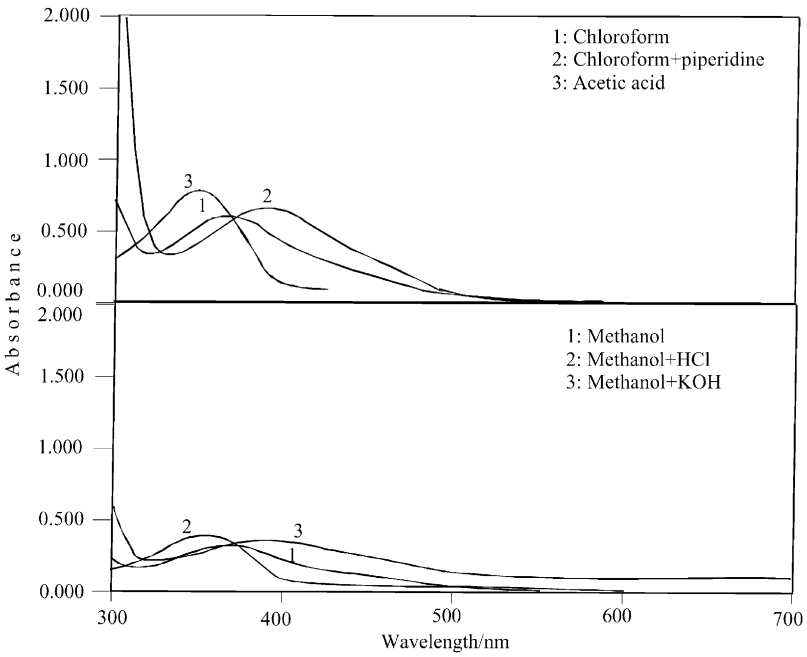


Fig. 2. Absorption spectra of dye **9** in acidic and basic solutions.

As in apparent in Table 3, the introduction of electron-withdrawing chloro and nitro groups and electron-donating methyl and methoxy groups in the benzene rings resulted in bathochromic effects in DMSO, DMF, acetonitrile, acetic acid and chloroform except compound **5** (*p*-(3-nitrophenylazo)calix[6]arene). Electron-withdrawing nitro (*m*-) group into the benzene rings gave hypsochromic effects in all solvents. Also, electron-withdrawing chloro (*p*-) group and electron-donating methyl (*o*-, *m*-, *p*-) and methoxy (*p*-) groups into the benzene rings gave hypsochromic effects in methanol. Electron-withdrawing chloro and nitro groups into the benzene rings generally gave more bathochromic effects than electron-donating methyl and methoxy groups in DMSO, DMF, acetonitrile, acetic acid and chloroform. The position of all groups did not show a regular variation in all solvents.

4. Conclusions

The present paper reports on the synthesis, characterization and their absorption spectra of a series of azocalix[6]arene compounds **1**–**12**. We have shown that bathochromic and hypsochromic effects produced is dependent on the *o*-, *m*-, *p*-substitue aniline derivatives diazo-coupling the calix[6]arene units. We have observed results the effect of varying pH and solvent upon absorption ability of azocalixarenes substituted with electron-donating and electron-withdrawing groups at their *o*-, *m*-, *p*-positions.

Further work of the complexation properties of these new azocalixarenes are currently under investigation and will be presented in full in due course. It was shown that the mechanism of complexation is based on the interaction between metal cations and azo-groups. It is important to note that the conformation of the calix[*n*]arenes, and the cooperativity and allosteric effects of the functionalities play important role in two-phase extraction systems. The variety of hydrogen bonding motifs that occur in the studied calix[*n*]-arene derivatives may be of considerable importance for the future design of novel calix[*n*]arene based receptors, carriers or supramolecular structure. Azocalix[*n*]arenes are excellent dyes for textile fiber.

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