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Azocalixarenes. 1: synthesis, characterization and investigation of the absorption spectra of substituted azocalix[4]arenes

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Abstract

A series of novel azocalix[4]arene dyes (**1–12**) were prepared by linking *o*-, *m*-, *p*-chloroaniline, *o*-, *m*-, *p*-nitroaniline, *o*-, *m*-, *p*-toluidine, *m*-, *p*-anisidine and aniline to calix[4]arene through a diazo-coupling reaction. These compounds were characterized by UV-vis, FT-IR and ^{1}H-NMR spectroscopic techniques and 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[4]arene. Concentration effects on the visible absorption maxima of the dyes are also reported.

Keywords: Calixarene; Azocalix[4]arenes; Calixarene dyes; Diazo-coupling reaction; Solvent effect; Substituent effect; Absorption properties

1. Introduction

Calixarenes are often described as "macrocycles with unlimited possibility" because of their versatility and utility as host molecules, which mostly comes from the ease in the synthesis of the basic platform and ready functionalization at lower and upper rims to construct variously modified three-dimensional structures [1]. Current studies on the synthesis of calixarene derivatives have promised the development of microcontact printing [2], ion selective electrodes [3] and electrochemical sensors for anions [4]. However, there is still an important need for systems that can exhibit colour changes due to ionic or molecular interactions. Of these azocalixarenes have been mainly studied calixarenes bridging phenylazo moieties on the upper rim [5,6] and lower rim [7], double azocalixarenes [8] and azocalixcrowns [9].

In contrast, the incorporation of carbocyclic and heterocyclic chelating agents such as for example 4-*n*-butylaniline, 4-(phenylazo)aniline, 4-aminoacetanilide, *N'*-2-thiazol-2-ylsulfonylamide and 2-aminothiazol to the lower rim of calixarene [10] have a special interest in the complexation of transition metal cations [11].

Many patents and papers describe the synthesis and dyeing properties of phenylazopyrazolone disperse dyes [12]. In recent years, the synthesis and comparative tinctorial behaviour of some

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3-methyl-1-(3′,5′-dipiperidino-s-triazinyl)-5-pyrazolone substituted hetarylazopyrazolone derivatives have been reported [13].

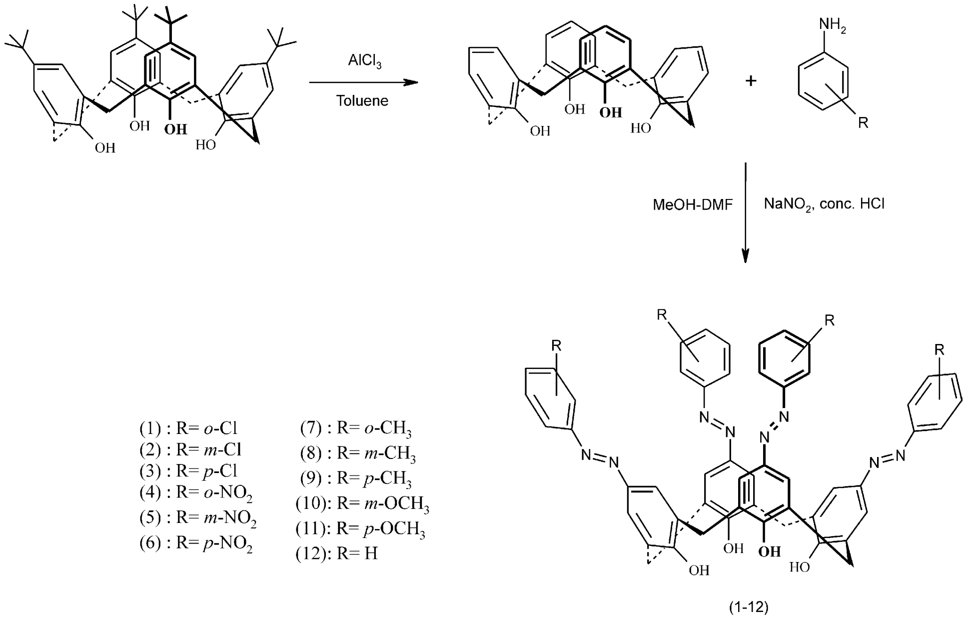
Recent work by the author has described the preparation of the new azocalixarenes that were synthesized using calix[n]arenes and phenols with various amines [14–16]. Previous studies have confirmed that in the presence of Cu^{2+}, Ni^{2+}, Co^{2+} ions, Fe^{3+} can be extracted selectively using calixarenes. We have examined both the selective extraction of Fe^{3+} ion from the aqueous phase into the organic phase [17] as well as the liquid–liquid extraction of transition metal cations [18] using diazo-coupled calixarenes.

As we are interested in the development of a new class of chromoionophore dyes, the aim of the present work was to design calix[4]arenes which contain both an aniline moiety as an electron-donating or electron-withdrawing group and an azophenol moiety to provide colour. The incorporation of an aniline subunit was chosen because of its potential double-site wavelength shift abilities. This led to the preparation of 12 new diazo-coupled calix[4]arenes substituted by substituted aniline derivative subunits **1–12** (Scheme 1).

2. Experimental

2.1. General

All solvents and compounds were commercial grade reagents that were used without further purification. Melting points were measured using an Electrothermal IA9100 digital melting point apparatus in capillaries sealed under nitrogen and are uncorrected. ^1H 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. Osmometric molecular mass determinations were carried out on a Knauer vapor pressure osmometer at concentrations of



(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

(1-12)

Scheme 1. *o*-, *m*-, *p*-substituted azocalix[4]arene derivatives.

ca.10^{-3} mol/L in DMSO. The elemental analysis was performed in the TUBITAK Laboratory (Center of Science and Technology Research of Turkey).

Solvent of crystallization was retained in some of the analytical samples and affected the elemental analysis. In such cases, best fits between the analytical values and appropriate fractional increments of solvents were used.

2.2. Preparation of the ligands

p-tert-Butylcalix[4]arene [19] and calix[4]arene [20] were synthesized as described by a previously reported method.

2.3. Preparation of phenylazocalix[4]arene dyes (**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[4]arene (**2**), *p*-(4-chlorophenylazo)calix[4]arene (**3**), *p*-(2-nitrophenylazo)calix[4]arene (**4**), *p*-(3-nitrophenylazo)calix[4]arene (**5**), *p*-(4-nitrophenylazo)calix[4]arene (**6**), *p*-(2-methylphenylazo)calix[4]arene (**7**), *p*-(3-methylphenylazo)calix[4]arene (**8**), *p*-(4-methylphenylazo)calix[4]arene (**9**), *p*-(3-methoxyphenylazo)calix[4]arene (**10**), *p*-(4-methoxyphenylazo)calix[4]arene (**11**) and *p*-(phenylazo)calix[4]arene (**12**) were obtained using the same method in 61–91% 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[4]arene (**1**)

A solution of 2-chlorophenyldiazonium chloride, which was prepared from 2-chloroaniline (1.28 g, 10 mmol), sodium nitrite (0.69 g, 10 mmol) and conc. HCl (7 mL) in water (25 mL), was added slowly to a cold (5 °C) solution of calix[4]arene (1.0 g, 2.36 mmol) and sodium acetate trihydrate (4.08 g, 30 mmol) in H_2O–DMF (26 mL, 5:8, v/v) to give a dark orange suspension. After standing for 2 h at room temperature, the suspension was acidified with aqueous HCl (150 mL, 0.25%) and the mixture was then warmed to 60 °C for 30 min to give **1** (yield, 1.67 g, 72%) as a dark orange solid, which was filtered and washed with water and MeOH. A sample for analysis was obtained as follows: **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 for 30 min and then cooled. The resulting solid was filtered, washed with water, and dried. Recrystallization from DMF/H_2O mixture gave a dark orange product (yield, 1.50 g (65%), m.p. dec. > 230 °C).

3. Results and discussion

3.1. Synthesis and characterizations

In this work, 12 new azo compounds (and their absorption properties) were synthesised from *o*-, *m*-, *p*-chloroaniline, *o*-, *m*-, *p*-nitroaniline, *o*-, *m*-, *p*-toluidine, *m*-, *p*-anisidine and aniline. These compounds (**1–12**) are shown in Scheme 1.

Calixarenes have been widely used as three-dimensional building blocks for the construction of artificial molecular receptors capable of recognizing neutral molecules, cations and, more recently, anions [8,9,21–23]. Thus, the chromogenic compounds reported here were designed to take advantage of the well-established binding interactions and spectroscopic properties of chromogenic molecules. The synthesis of compounds **1–12** (Scheme 1) was based on previously published procedures [19,20,24], while the two tautomeric forms of azocalix[4]arenes from **1** to **12** (Scheme 2) are reported for the first time.

Previously, the synthesis of calix[4]arenes was performed using the method of Gutsche et al. [19,20].

In previous work, we investigated the azo coupling reactions of calix[*n*]arene with substituted benzenediazonium chlorides [10,14–16]. The series of 12 novel azocalix[4]arene derivatives described herein were synthesised according to the method described by Morita et al. [24]. All

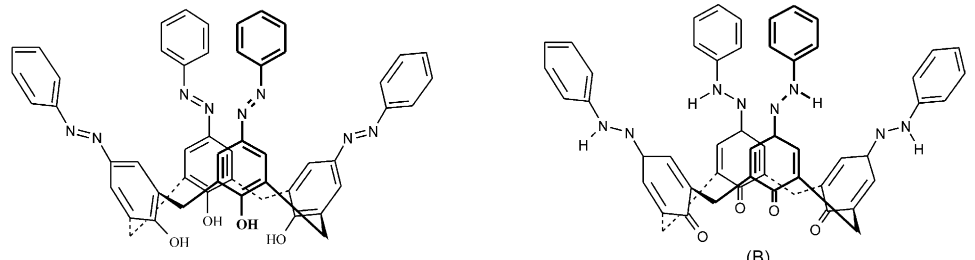
Table 1
Spectral data for coumpound **1–12**

Compound no.	IR (cm^{-1}) in KBr						^{1}H NMR (δ, ppm)			
	$\nu_{\text{O-H}}$	$\nu_{\text{C-H(aro.)}}$	$\nu_{\text{C-H(alip.)}}$	$\nu_{\text{C=C}}$	$\nu_{\text{N=N}}$	$\nu_{\text{C-O}}$	Aro-H	Alip-H	X-H	Solvent
1	3214	3063 3027	2946	1679	1616	1063	6.83–8.23 (24H, m)	2.11 and 4.23 (8H, s)	10.95 (OH, b) 14.17 (NH, b)	DMSO-d_6
2	3339	3105 3071	2938	1696	1598	1071	6.78–8.00 (24H, m)	2.24 and 4.17 (8H, s)	11.14 (OH, b) 14.34 (NH, b)	DMSO-d_6
3	3223	3107 3045	2955	1714	1625	1107	7.22–7.86 (24H,m)	2.18 and 4.08 (8H, s)	11.51 (OH, b) 14.18 (NH, b)	DMSO-d_6
4	3200	3089 3036	2946	1688	1607	1071	7.02–8.05 (24H, m)	2.17 and 4.17 (8H, s)	11.45 (OH, b) 13.87 (NH, b)	DMSO-d_6
5	3223	3090 3036	2946	1696	1607	1089	7.17–8.35 (24H, m)	2.24 and 4.15 (8H, s)	10.88 (OH, b) 13.56 (NH, b)	DMSO-d_6
6	3268	3107 3045	2964	1679	1590	1116	7.13–8.11 (24H, m)	2.09 and 4.17 (8H, s)	11.67 (OH, b) 14.57 (NH, b)	DMSO-d_6
7	3241	3089 3018	2946	1696	1607	1107	7.00–7.79 (24H, m)	2.24 and 4.17 (8H, s) 2.09 and 2.71 (12H, s)	11.58 (OH, b) 14.32 (NH, b)	DMSO-d_6
8	3241	3089 3036	2946	1696	1594	1089	6.70–7.89 (24H, m)	2.09 and 4.15 (8H, s) 2.24 (12H, s)	10.82 (OH, b) 13.87 (NH, b)	DMSO-d_6
9	3232	3098 3036	2938	1697	1589	1089	7.00–7.80 (24H, m)	2.24 and 4.19 (8H, s) 2.17 and 2.39 (12H, s)	11.48 (OH, b) 14.17 (NH, b)	DMSO-d_6
10	3232	3107 3045	2964	1696	1625	1196	6.42–7.71 (24H, m)	2.09 and 4.14 (8H, s) 3.71 (12H, s)	10.93 (OH, b) 14.21 (NH, b)	DMSO-d_6
11	3232	3089 3036	2955	1688	1587	1125	6.78–7.83 (24H, m)	2.23 and 4.21 (8H, s) 3.62 (12H, s)	11.2 (OH, b) 14.17 (NH, b)	DMSO-d_6
12	3200	3107 3054	2961	1679	1589	1116	7.00–8.02 (28H, m)	2.10 and 4.17 (8H,s)	11.03 (OH, b) 13.97 (NH, b)	DMSO-d_6

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	$C_{52}H_{36}Cl_4N_8O_4$	979	65	63.82	64.34	3.71	3.89	11.45	11.11	Dec. > 230
2	$C_{52}H_{36}Cl_4N_8O_4$	979	85	63.82	64.41	3.71	3.87	11.45	10.98	Dec. > 200
3	$C_{52}H_{36}Cl_4N_8O_4$	979	87	63.82	64.44	3.71	3.87	11.45	10.93	Dec. > 200
4	$C_{52}H_{36}N_{12}O_{12}$	1021	64	61.18	62.55	3.55	3.71	16.46	15.97	Dec. > 210
5	$C_{52}H_{36}N_{12}O_{12}$	1021	81	61.18	62.61	3.55	3.63	16.46	15.91	Dec. > 220
6	$C_{52}H_{36}N_{12}O_{12}$	1021	79	61.18	62.57	3.55	3.69	16.46	15.95	Dec. > 225
7	$C_{56}H_{48}N_8O_4$	897	64	74.98	75.63	5.39	5.54	12.49	11.91	Dec. > 210
8	$C_{56}H_{48}N_8O_4$	897	87	74.98	75.56	5.39	5.58	12.49	11.95	Dec. > 220
9	$C_{56}H_{48}N_8O_4$	897	61	74.98	75.51	5.39	5.63	12.49	12.09	Dec. > 200
10	$C_{56}H_{48}N_8O_8$	961	91	69.99	70.38	5.03	5.22	11.66	11.26	Dec. > 220
11	$C_{56}H_{48}N_8O_8$	961	88	69.99	70.47	5.03	5.29	11.66	11.18	Dec. > 200
12	$C_{52}H_{40}N_8O_4$	840	81	74.27	74.66	4.79	4.93	13.32	12.87	Dec. > 200



(A)
azo-enol

(B)
keto-hydrazo

Scheme 2. The tautomeric forms of 4-(phenylazo)calix[4]arene (**12**).

reactions proceeded smoothly producing the corresponding azo compounds in good yields. All aniline derivatives reacted quantitatively with an equimolecular amount of calix[4]arenes.

The synthetic utility of diazo-coupling phenolic compounds is well known and can occur across the calixarenes upper rim. Thus, calix[4]arene was treated with aniline derivatives in aqueous DMF to give azocalix[4]arene **1-12** in quantitative yield which was confirmed by the appearance of an azo band at 1625–1589 in the FT-IR spectra of these compounds. The new compounds were characterized using ^{1}H-NMR, FT-IR, and elemental analysis.

The FT-IR spectra of all compounds (**1–12**) showed a weak band within the range 3339–3200 cm^{-1} corresponding to ν_{OH}. The low value reveals that the -OH group was involved in intramolecular H-bonding. The FT-IR spectra also show a weak band or shoulder located at 3107–3018 cm^{-1} which was assigned to aromatic C-H, asymmetrical stretching vibration of the $N=N$ group leading to the band located in the 1600–1500 cm^{-1} region, while the other stretching vibration of the $N=N$ group in the range 1625–1589 cm^{-1} was masked by the intense bands due to ring vibration.

The azocalix[4]arene derivatives (**1–12**) showed characteristic absorption patterns. The appearance of the azocalix[4]arene absorption band at a relatively high wavelength may be attributed to the presence of an electron-withdrawing group, nitro or chloro. The electronic absorption spectra of azocalix[4]arene derivatives (**1–12**) exhibited one absorption band and a shoulder in the range 300–700 nm corresponding to π–π* and n–π* transitions which is in accordance with typical diazo spectra.

The visible spectral properties of the azocalix[4]arene derivatives were compared with *o*-, *m*-, *p*-substituents. Electron-withdrawing and electron-donating substituents in the aryl ring exerted a bathochromic effect.

The azocalix[4]arenes (**1–12**) may exist in two possible tautomeric forms, namely an azo-enol form A and keto-hydrazo B (Scheme 2). Deprotonation of the two tautomers leads to a common anion. The infrared spectra of all compounds (in KBr) showed broad -OH bands at 3339–3200 cm^{-1} and C-O bands at 1196–1063 cm^{-1}. It can be suggested that these compounds do not exist as the keto-hydrazo form in the solid state.

The structures of **1–12** were examined in solution by high-resolution NMR. The ^{1}H-NMR spectrum measured in DMSO-d_6 at 25 °C showed broad bands of hydroxy and imine protons ($\delta = 10.82$–11.67 (OH) and $\delta = 13.56$–14.57 (NH), respectively). Also, the ^{1}H-NMR spectra of compounds (**1–12**) in DMSO-d_6 showed single bands at $\delta = 2.09$–2.24 (–CH$_2$–) and $\delta = 4.08$–4.23 (–CH$_2$–). These findings suggest that the compounds may exist as a mixture of the two tautomeric forms in DMSO-d_6.

3.2. Solvent effect

The absorption spectra of azocalix[4]arenes **1–12** were recorded in various solvents at a concentration of $\sim 10^{-6}$–10^{-8} M; the results are summarised in Table 3. The visible absorption spectra of the compounds were found to exhibit strong

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

Compound no.	DMSO		DMF		Acetonitrile		Methanol		Acetic acid		Chloroform	
	conc.	dil.	conc.	dil.	conc.	dil.	conc.	dil.	conc.	dil.	conc.	dil.
1	407	401	385	384	373	371	370	369	350	350	360	363
	458 s	455 s	441 s	441 s	436 s	435 s			382 s	480 s	454 s	455 s
2	386	386	384	384	354	357	352	350	347	346	350	350
	464 s	464 s	463 s	463 s	441 s	445 s			432 s	430 s	435 s	435 s
3	415	415	408	408	396	396	399,	399,	394	393	391	390
	490 s	490 s	488 s	489 s	476 s	476 s	480 s	480 s				
4	371	380	370	375	376	377	367	368	347	344	358	356
	455 s	458 s	455 s	457 s	454 s	455 s					448 s	445 s
5	389	390	388	387	382	382	387	388	383	383	360	363
	452 s	453 s	450 s	450 s								
6	400	406	421	425	357	357	371,	381,	350	349	351	351
					422 s	422 s	425 s	430 s	422 s	421 s	424 s	424 s
7	367	367	367	367	354	354	356	357	353	352	351	350
	427 s	427 s	427 s	427 s	427 s	427 s			429 s	427 s	427 s	425 s
8	367	367	367	367	356	355	358,	360,	350	350	352	351
	438 s	438 s	438 s	438 s	436 s	436 s	437 s	438 s	436 s	436 s	436 s	435 s
9	383	383	379	385	371	371	376,	377,	349	347	352	351
	441 s	442 s	439 s	435 s	410 s	410 s	420 s	419 s				
10	386	384	382	381	362	362	369,	370,	350	347	353	355
	435 s	435 s	432 s	430 s			422 s	422 s	422 s	420 s	420 s	421 s
11	387	387	387	385	363	361	371,	369,	354	354	358	358
	440 s	440 s	439 s	436 s	432 s	430 s	435 s	432 s				
12	371	375	371	370	347	348	348,	349,	340	341	342	342
	446 s	448 s	446 s	445 s	430 s	431 s	430 s	430 s	419 s	419 s	434 s	434 s

[a] s: shoulder

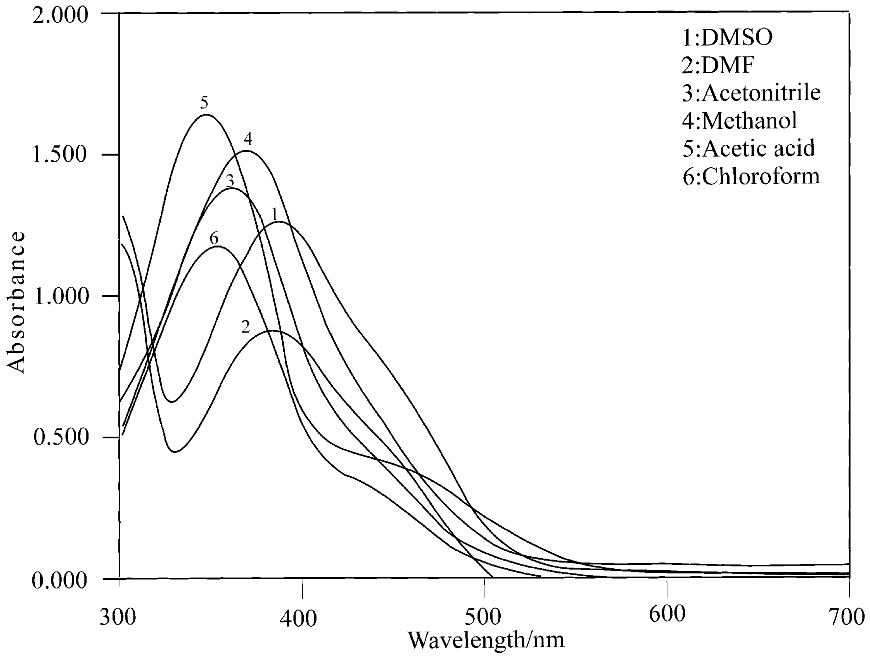


Fig. 1. Absorption spectra of dye **10** in various solvents.

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

Compound no.	Chloroform	Chloroform + piperidine	Acetic acid	Methanol	Methanol + KOH	Methanol + HCl	DMSO	DMSO + piperidine	DMF	DMF + piperidine
1	363 455 s	419	350 480 s	369	396	342	401 455 s	490, 420 s	384 441 s	470, 400 s
2	350 435 s	383, 444 s	346 430 s	350	410	330	386 464 s	455, 488 s	384 463 s	425, 480 s
3	390	406, 483 s	393	399, 480 s	519, 396 s	398, 479 s	415 490 s	579, 429 s	408 489 s	578, 428 s
4	356 445 s	375, 450 s	344	368	391	357	380 458 s	438, 478 s	375 457 s	385, 463 s
5	363	377, 439 s	383	388	394, 465 s	381	390 453 s	429, 476 s, 576 s	387 450 s	392, 463 s, 576 s
6	351 424 s	386, 444 s	349 421 s	381, 430 s	393, 445 s	353	406	423	425	423
7	350 425 s	364, 426 s	352 427 s	357	410	353	367 427 s	482, 382 s	367 427 s	369, 427 s
8	351 435 s	367, 438 s	350 436 s	360, 438 s	405, 450 s	353, 436 s	367 438 s	469, 377 s	367 438 s	370, 440 s
9	351	385, 436 s	347	377, 419 s	384, 436 s	347	383 442 s	417, 456 s	385 435 s	413, 448 s
10	355 421 s	377, 427 s	347 420 s	370, 422 s	397, 448 s	371, 420 s	384 435 s	400, 451 s	381 430 s	387, 444 s
11	358	377, 428 s	354	369, 432 s	379, 438 s	358	387 440 s	388, 451 s	385 436 s	385, 440 s
12	342 434 s	377, 446 s	341 419 s	349, 430 s	392, 460 s	324, 400 s	375 448 s	393, 463 s	370 445 s	385, 454 s

[a] s: shoulder

solvent dependency, which did not show regular variation with the polarity of the solvents.

Strong evidence for the existence of these compounds existing in an equlibrium is provided by the isosbestic points in the visible spectra of, for example, compound **10** in different solvents (Fig. 1). This equilibrium may exist between tautomeric forms. The equilibrium depends on the basicity of the solvents used; in proton accepting solvents such as DMSO, DMF, acetonitrile and methanol, the compounds displayed a red shift of $\lambda_{\max}$. In a proton donating solvent such as acetic acid, the $\lambda_{\max}$ of the compounds did not significantly change with respect to the absorption spectra in chloroform with the exception of compound **2** and compound **4**.

The $\lambda_{\max}$ of the compounds showed large bathochromic shifts 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 $\lambda_{\max}$ of the compounds in methanol also showed bathochromic shifts when 0.1 M KOH was added. These findings indicate that compounds **1–12** exist in the anion form in chloroform + piperidine, DMSO + piperidine, DMF + piperidine and methanol + KOH.

The effect of concentration of the compound on absorption maxima was examined (Table 3). The $\lambda_{\max}$ of all compounds did not change with compound concentration which also indicates that azocalix[4]arenes exist in their tautomeric form in all solvents used.

3.3. Substituent effects

As is apparent in Table 3, the introduction of electron-withdrawing nitro and chloro groups and electron-donating methoxy and methyl (*p*-) groups in the benzene rings resulted in bathochromic shifts in all solvents. However the introduction of electron-donating methyl (*o*-, *m*-)

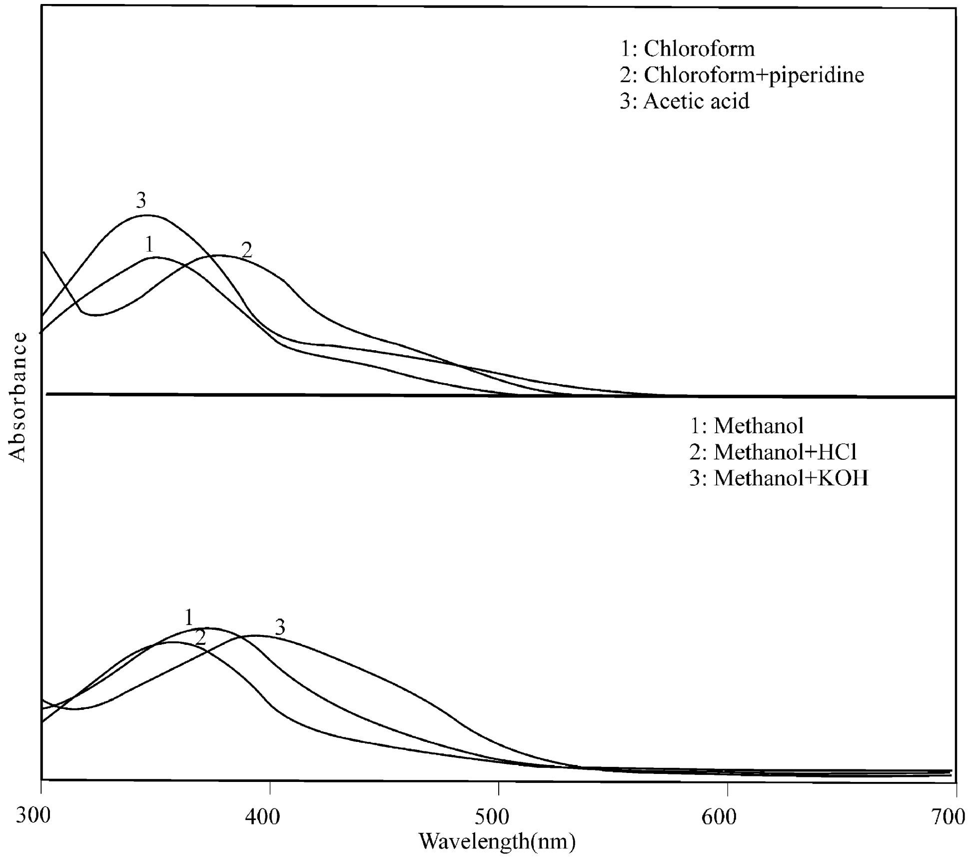


Fig. 2. Absorption spectra of dye **10** in acidic and basic solutions.

groups into the benzene rings gave hypsochromic shifts in DMSO and DMF but produced bathochromic shifts in acetonitrile, methanol, acetic acid and chloroform. The introduction of nitro groups into the benzene rings imparted the greatest bathochromic shift of all groups. The position of all groups did not show a regular variation in all solvents.

The visible absorption maxima (λ_{max}) in all solvents are given Table 3. Inspection of Table 3 shows that the azocalix[4]arene derivatives **1**–**6** derived from chloro- and nitro- anilines containing electron-withdrawing chloro- and nitro- groups and the azocalix[4]arenes (**1**–**12**) not give uniform bathochromic shifts of about 9–48 nm relative to the corresponding the azocalix[4]arene derivatives **7**–**11** from methyl- and methoxy- anilines containing one electron-donating methyl- and methoxy- groups. Thus azocalix[4]arenes **1** and **3** with an *o*- and *p*- chloro substituent in the diazo component, absorbed at 407 and 415 nm. When the chloro group was in the meta position (**2**), the absorption shifted to 386 nm in DMSO.

4. Conclusions

Diazo-coupling reactions are shown in Scheme 1. This pathway is the most convenient to give the best yield of diazo-coupling calixarene compounds. We studied the diazo-coupling reactions of calix[4]arene with benzenediazonium chloride, *o*-, *m*-, *p*-chloroaniline, *o*-, *m*-, *p*-nitroaniline, *o*-, *m*-, *p*-toluidine, *m*-, *p*-anisidine and aniline.

Twelve new calixarene-based receptors with hydrogen-bonding groups immersed in a large cavity have been synthesized. The synthesis of all of the diazo-coupled compounds was achieved using the method of Morita [24]. These reactions produce the corresponding azo compounds in good yield.

In contrast, the azo groups of these compounds are interesting because they act as microcontact printing sites as well as chromophores. We are currently working on those azo groups containing calix[4]arene derivatives and in particular their binding properties for metal ions.

o-, *m*-, *p*-Substituted groups dissociate progressively in solution with increasing pH, so forming azo-enol form and keto-hydrazo form species, with characteristic changes in the visible absorption spectra. The azocalix[4]arene derived from calix[4]-arene and substituted aniline shows a pronounced colour change from chloro-, nitro-, methyl- and methoxy—to an orange in dry $CHCl_3$ on addition of up to 0.5% water, due to the formation of the mono-anion, and can be used as analytical indicators for detecting low levels of water in solvents. As both the neutral and mono-anionic forms of azocalix[4]-arene derives are non-fluorescent, these compounds can be used as pH indicators.

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