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Azocalixarenes. 4: synthesis, characterization and investigation of the absorption spectra of hetarylazo-substituted calix[6]arenes

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Abstract

Synthesis of seven novel hetarylazocalix[6] arene dyes was achieved by diazotisation of seven different heterocyclic amines using nitrosyl sulphuric acid, coupling with calix[6]arene. Hetarylazocalix[6]arene dyes were characterized based on FT-IR and ^{1}H-NMR spectroscopic techniques as well as elemental analysis. The absorption spectra of the dyes are discussed, both the effect of varying pH and solvent upon the absorption ability of azocalixarenes. Absorption maxima of the prepared dyes showed large bathochromic effects in comparison with analogues dyes containing carbocyclic amine residue. The colour of the azocalixarene dyes is discussed with respect to the nature of the heterocyclic ring and substituents there in. Concentration effects on the visible absorption maxima of the dyes are also reported.

Keywords: Calixarene; Hetarylazocalix[6]arenes; Heterocyclic amines; Diazo-coupling reaction; Solvent effect; Substituent effect; Absorption properties

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1. Introduction

Calixarenes, which are cyclic products in the phenol–formaldehyde condensation reaction, possess an inner hydrophobic cavity [1]. They are receiving increasing attention in the field of supramolecular chemistry because of simple preparations, easy modifications, and unique properties. Particularly calix[4]arenes have been frequently used as building blocks for the construction of highly sophisticated host molecules [2]. The combination of calix[4]arenes functionality with transition metals may provide novel organometallic materials, which might realize unique supramolecular catalysis [3], by utilizing a spatially confined environment.

Azocalix[n]arenes are one of the most useful and widely employed ligands for transition metal complexes, many of which display excellent activity and selectivity in homogenous catalytic reactions. Among these works, azocalixarenes have been mainly studied: calixarenes bridging phenylazo moieties on the upper rim [4,5] and lower rim [6], double azocalixarenes [7], azocalixcrowns [8].

The inner space of azocalixarenes molecules provides a unique microenvironment to the included guest species. Recently, the dyes behavior of

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azocalixarene species such as carbocyclic amines included in *p*-position of calixarenes and absorption spectra has been reported [9].

A chromogenic calix[*n*]arene substituted by phenylazo groups have beeen previously characterized and were used in the present work to study their absorption spectra with variety pH and different solvents. The presence of azo-chromophores in these compounds allow detection of changes of optical absorption in the visible range resulting from the interaction of heterocyclic ring with the π-electrons of the azo-chromophores [10,11].

Although a lot chromogenic reagents for transition metals detection have been reported [12,13], none of the reagents was prepared by attaching a chromogenic moiety to a platform of a macrocyclic compound, such as calixarene. 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 metal ions is one of the most remarkable features, this makes them suitable as specific receptors. In the past years, many calixarene derivatives have been synthesized to achieve highly selective ligands for alkali [14], alkaline earth [15], and transition metals ions [16]. However, very few calixarene derivatives were designed as chromogenic reagents for the determination of Ni^{2+}.

In this work, based on previous experience [10,11,17], our aim was to synthesize azocalixarenes and their hetarylazo derivatives by substituting different rings on lower rim and to investigate both the effect of varying pH and solvent upon the absorption ability of hetarylazocalix[6]arenes.

2. Experimental

2.1. General

All solvents and compounds were commercial grade reagents that were used without further purification. Melting points were taken on 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 FT-IR 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 ca.10^{-3} mol/L in DMSO. The elemental analysis were 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[6]arene [18] and calix[6]arene [19] were synthesized as described by a previously reported method.

2.2.1. Preparation of hetarylazocalix[6]arene dyes (**1–7**)

Diazotisation of the various heterocyclic amines was effected with nitrosyl sulphuric acid. A typical procedure is that described below used for 2-aminobenzothiazole. *p*-(6-Chloro-2-benzothiazolylazo)calix[6]arene (**2**), p-(2-benzimidazolylazo)calix[6]arene (**3**), *p*-(5-methyl mercapto-1,2,4-triazol-3-ylazo)calix[6]-arene (**4**), *p*-(5-methyl-3-isoxazolylazo)calix[6]arene (**5**), *p*-(1,3,4-thiadiazol-2-ylazo)calix[6]arene (**6**), *p*-(1,3,4-thiadiazol-2-thiol-5-ylazo)calix[6]arene (**7**) were obtained using the same method in 60–96% yield. The obtained compounds were purified by crystallization using the same solvent (DMF–H_2O) and were then analyzed. Characterization data are shown in Tables 1 and 2.

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

2-Amino-6-chlorobenzothiazole (2.40 g, 16 mmol) was dissolved in hot glacial acetic acid (10 ml) and was rapidly cooled in an ice-salt bath to −5 °C. The liquor was then added in portions during 30 min to a cold solution of nitrosyl sulphuric acid (prepared

Table 1
Spectral data for dyes **1–7**

Dye no.	FT-IR (cm^{-1}) in KBr						^{1}H-NMR (δ, ppm)			
	$\nu_{\text{O-H}}$	$\nu_{\text{C-H(aro.)}}$	$\nu_{\text{CH (alip.)}}$	$\nu_{\text{C=C}}$	$\nu_{\text{N=N}}$	$\nu_{\text{C-O}}$	Aro-H	Alip-H	X-H	Solvent
1	3223	3089, 3036	2964	1688	1607	1089	7.21–8.15 (36H, m)	2.25 and 4.19 (12H, s)	11.57 (OH, b) 14.21 (NH, b)	DMSO-d_6
2	3214	3080, 3018	2929	1643	1589	1080	7.22–8.16 (30H, m)	2.09 and 4.15 (12H, s)	11.61 (OH, b) 14.32 (NH, b)	DMSO-d$_6$
3	3321	3071	2964	1705	1625	1107	7.22–7.75 (36H, m)	2.21 and 4.22 (12H, s)	7.02 and 9.61 (6H, NH,b) 10.94 (OH, b) 14.18 (NH, b)	DMSO-d_6
4	3357	3080, 3036	2920	1661	1580	1116	7.22–7.61 (12H, m)	2.11 and 4.18 (12H, s) 2.85 (18H, s)	6.17 and 12.17 (6H, NH, b)) 10.75 (OH, b) 13.80 (NH, b	DMSO-d_6
5	3200	3089, 3036	2911	1643	1571	1125	6.10–7.72 (18H, m)	2.20 and 4.12 (12H, s) 2.45 (18H, s)	11.42 (OH, b) 14.27 (NH, b)	DMSO-d_6
6	3200	3071, 3018	2920	1661	1589	1089	7.22–9.69 (18H, m)	2.25 and 4.21 (12H, s)	11.87 (OH, b) 14.54 (NH, b)	DMSO-d_6
7	3259	3054	2946	1643	1571	1125	7.22–7.61 (12H, m)	2.12 and 4.18 (12H, s)	2.37 (6H, SH, b) 11.62 (OH, b) 14.48 (NH, b)	DMSO-d_6

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

Table 2
Element analysis of dyes **1**–**7**

Dye no.	Molecular formula	Molecular mass	Yield %	C %		H %		N %		S %		Melting point °C
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
1	$C_{84}H_{54}N_{18}O_6S_6$	1602	60	62.92	63.21	3.37	3.41	15.73	15.54	11.98	11.68	Dec. > 300
2	$C_{84}H_{48}Cl_6N_{18}O_6S_6$	1809	61	55.72	55.94	2.65	2.73	13.93	13.78	10.61	10.44	Dec. > 340
3	$C_{84}H_{60}N_{24}O_6$	1500	96	67.20	67.44	4.00	4.11	22.40	22.23	–	–	Dec. > 340
4	$C_{60}H_{54}N_{30}O_6S_6$	1482	64	48.58	48.81	3.64	3.69	28.34	28.17	12.96	12.75	Dec. > 290
5	$C_{66}H_{54}N_{18}O_{12}$	1290	89	61.39	61.53	4.19	4.25	19.53	19.34	–	–	Dec. > 295
6	$C_{54}H_{36}N_{24}O_6S_6$	1308	85	49.54	49.84	2.75	2.83	25.69	25.56	14.68	14.60	Dec. > 280
7	$C_{54}H_{36}N_{24}O_6S_{12}$	1500	64	43.20	43.38	2.40	2.46	22.40	22.30	25.60	25.51	Dec. > 300

from sodium nitrite (1.10 g) and concentrated sulphuric acid (15 mL at 70 °C)). The mixture was stirred for an additional 1 h at 0 °C. After diazotisation was complete, the diazo liquor was slowly added to a vigorously stirred solution of calix[6]arene (1.5 g, 2.36 mmol) in DMF–H_2O (30 mL, 8:5, v/v). The pH of the reaction mixture was maintained at 7–8 by simultaneous addition of solid sodium carbonate in portions. The mixture was then stirred for 1 h at 0–5 °C. The progress of the reaction was followed by TLC using a DMF–H_2O mixture (8:5, v/v) as the developing solvent and silica gel TLC plates as the stationary phase. The resulting solid was filtered, washed with cold water and dried. Recrystallization from DMF–H_2O mixture gave a brown product (yield: 60%, m.p: dec. > 300 °C).

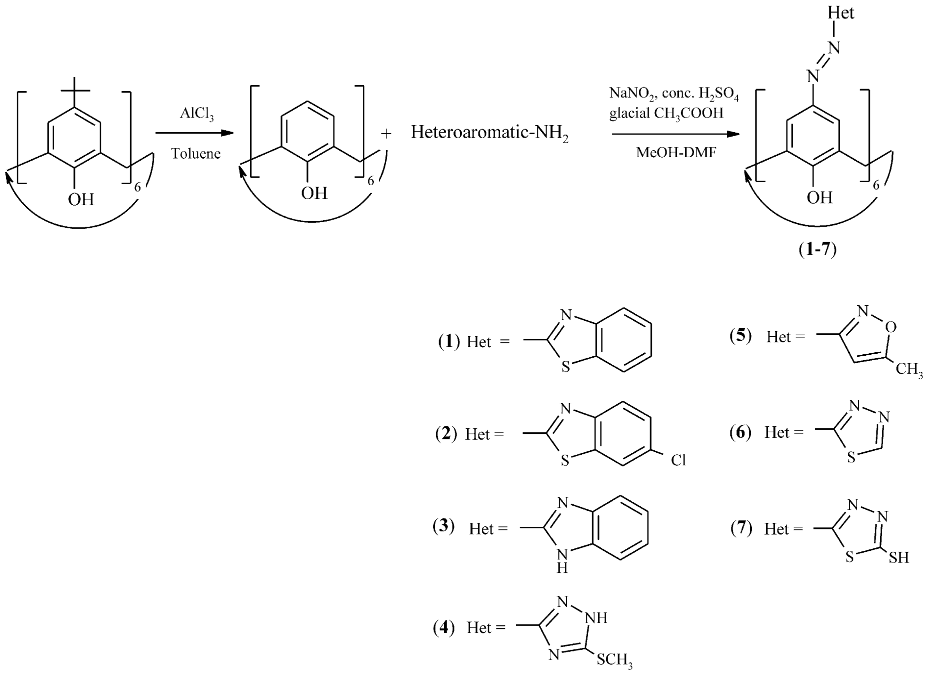
3. Results and discussion

3.1. Synthesis and characterizations

Much attention has been paid in recent years to diazo-coupling techniques and the design and synthesis of new azocalixarene dye reagents with a high coupling ability and an electrophiles and even cations in views of environmental protection. Azocalixarene dyes are effective and can be extensively modified to make other dyes. In this regard, we now report seven novel different hetarylazo rings calix[6]arene derivatives outlined in Scheme 1. In this work, synthesis of all novel hetarylazocalix[6]arene dyes was achieved by diazotisation of seven heterocyclic amines using nitrosyl sulphuric acid, coupling with calix[6]arene. Hetarylazocalix[6]arene dyes were characterized based on FT-IR and ^{1}H-NMR spectroscopic techniques as well as elemental analysis. The absorption spectra of the prepared dyes are discussed, both the effect of varying pH and solvent upon the absorption ability of hetarylazocalix[6]arenes.

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 heterocyclic diazonium salt derivatives from heterocyclic amines in nitrosyl sulphuric acid, after then we employed 6 equivalent of these salts in 5:8 MeOH–DMF mixture with 1 equivalent of [6]arene to obtain the corresponding hetarylazocalix[6]arenes **1**–**7**. This general reaction described in Scheme 1. Work up of the reaction mixtures afforded the corresponding seven hetarylazocalix[6]arenes in 60–96% yield.

The hetarylazocalix[6]arenes (**1**–**7**) may exist in two possible tautomeric forms, namely an azo-enol form A and keto-hydrazo form B. The deprotonation of the two tautomers leads to a common anion. The FT-IR spectra of all dyes (**1**–**7**) showed a weak band within the range 3357–3200 cm^{-1} corresponding to $\nu_{\mathrm{O-H}}$. 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 3089–3018 cm^{-1} which was assigned to aromatic C–H, asymmetrical stretching vibration of the N=N group leading to the band located in 1600–1500 cm^{-1} region, while the other stretching vibration of the



Scheme 1. Hetarylazocalix[6]arene derivatives.

N=N group in the range 1625-1571 cm^{-1} was masked by the intense bands due to ring vibration. The other ν_{max} values of 2964–2911 cm^{-1} (aliphatic C–H), 1705–1643 cm^{-1} (C=C), 1125–1080 cm^{-1} (C–O) were recorded. The infrared spectra of all dyes (in KBr) showed a broad –OH bands at 3357–3200 cm^{-1} and 1125–1080 cm^{-1}. It can be suggested that these dyes exist as the azo-enol form in the solid state.

The structures of **1**–**7** were examined in solution using high-resolution NMR. The ^{1}H-NMR spectrum measured in DMSO-d_6 at 25 °C showed a singlet peak for methylene protons (–CH$_2$–) at δ 2.09–2.25 and 4.12–4.21, a singlet at 2.85 (–SCH$_3$), a singlet at 2.45 (–CH$_3$), a multiplet from 6.10–9.69 for aromatic protons (Aro-H), a broad peak at 10.75–11.87 (–OH), a broad peak at 13.80–14.54 (–NH), a broad peak at 7.02 and 9.61 (–NH) a broad peak at 6.17 and 12.17 (–NH) and a broad peak at 2.37 (–SH). At room temperature the broad peaks at 10.75–11.87 and 13.80–14.54 indicate that the dyes may be exist a mixture of tautomeric forms in DMSO-d_6.

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

3.2. Solvent effect

The absorption spectra of hetarylazocalix[6]arenes **1**–**7** were recorded in various solvents at a concentration of ~10^{-6}–10^{-8} M and these are all run at different concentrations; the results are summarized in Table 3. 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 visible absorption spectra of the dyes were found to exhibit strong solvent dependency, which did not show regular variation with the polarity of the solvents.

Typical absorption spectra of dye **1** shown in different solvents in Fig. 1. It was observed that the absorption spectra of the dye **1** in DMSO, DMF, chloroform + piperidine, methanol and acetonitrile significantly change with respect to the absorption spectra in acetic acid. Similarly, the absorption

Table 3
Influence of solvent on λ_{max} (nm) of dyes **1**–**7**

Dye no.	DMSO		DMF		Chloroform + piperidine		Methanol		Acetonitrile		Acetic aid	
	Conc.	Dil.	Conc.	Dil.	Conc.	Dil.	Conc.	Dil.	Conc.	Dil.	Conc.	Dil.
1	519, 451 s	525, 455 s	514, 450 s	521, 452 s	502, 430 s	503, 430 s	514, 448 s	515, 450 s	503, 431 s	502, 430 s	409	406
2	540, 439 s	540, 432 s	538, 431 s	538, 431 s	506, 426 s	504, 430 s	523, 430 s	523, 430 s	503, 415 s	502, 415 s	412	412
3	470, 444 s	469, 444 s	464, 440 s	464, 440 s	455, 436 s	453, 435 s	427, 445 s	427, 445 s	413, 454 s	414, 454 s	412, 450 s	411, 448 s
4	393, 471 s	392, 471 s	395, 472 s	394, 472 s	396, 471 s	396, 472 s	381, 460 s	383, 461 s	376, 451 s	373, 450 s	360, 440 s	358, 439 s
5	383, 444 s	384, 445 s	384, 445 s	383, 444 s	378, 440 s	378, 440 s	351, 427 s	366, 430 s	350, 411 s	350, 412 s	351, 415 s	350, 413 s
6	402, 500 s	403, 501 s	411, 500s, 541s	411, 502s, 542s	418, 494s, 540s	419, 494s, 541s	484, 400 s	483, 398 s	392, 475 s	392, 475 s	389	389
7	536	536	528	528	406, 504 s	406, 504 s	500	498	491	491	490	490

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

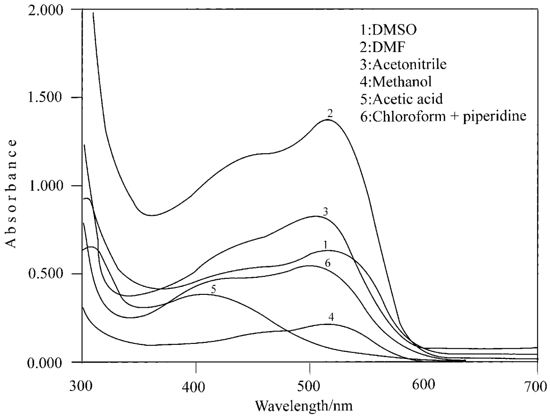
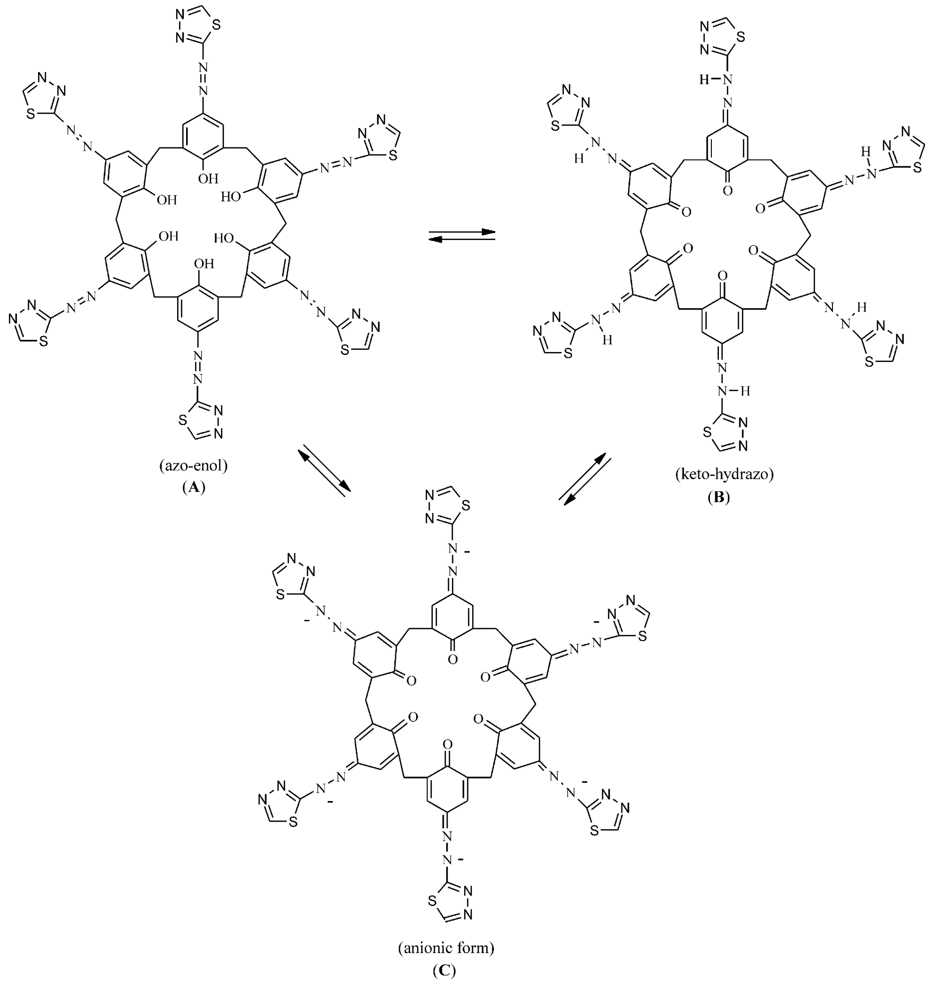


Fig. 1. Absorption spectra of dye **1** in various solvents.

spectra of all dyes in proton accepting solvents such as DMSO, DMF, chloroform + piperidine, methanol and acetonitrile significantly change with respect to the absorption spectra in acetic acid. The λ_{max} of the dyes in proton accepting solvents such as DMSO, DMF, chloroform + piperidine, methanol and acetonitrile displayed a red shift respect to the λ_{max} in acetic acid (e.g. for dye **1** λ_{max} is 409 nm in acetic acid, 519 nm in DMSO and 514 nm in DMF, for dye **2** λ_{max} is 412 nm in acetic acid, 540 nm in DMSO and 538 nm in DMF).

The hetarylazocalix[6]arene dyes may exist in two possible tautomeric forms. But dye **6** showed three absorption peaks in DMF and chloroform + piperidine. The equilibrium of dye **6** in DMF and



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

chloroform + piperidine may exist between tautomeric forms and anionic form. This indicates that dye **6** may exist in partly dissociated in DMF and chloroform + piperidine. Absorption peak at the longest wavelength of dye **6** may be a peak of anionic form (Scheme 2).

Heterocyclic based azo disperse dyes tend to show larger solvatochromic effects than phenylazo disperse dyes because of the increased polarity of the system, especially of the excited state. In previous works, similar effects for dyes containing chlorobenzothiazolyl, benzimidazolyl, methylmercaptotriazolyl, methylisoxazolyl, thiadiazolyl and thiolthiadiazolyl moieties have been reported for some derivatives of calix[4]arene dyes [10,17].

The λ_{max} of dye **5** showed large bathochromic shifts when a small of piperidine was added to each of its solutions in DMSO and DMF. The λ_{max} of dye **6** showed large bathochromic shift when a small of piperidine was added to its solution in DMSO (Table 4). The absorption spectra of dye **6** also showed three absorption peaks when a small of piperidine was added to its solution in DMSO. It can be suggested that dye **6** may exist in partly dissociated in DMSO + piperidine. The λ_{max} of dye **7** showed large hypsochromic shifts when a small of piperidine was added to each of its solutions in DMSO and DMF and absorption curves of the dye **7** resembled those in chloroform + piperidine. There was no significant change in the spectra when a small of piperidine was added to dyes **1**–**4** in DMSO and DMF (Table 4).

The λ_{max} of dyes **1--7** in methanol did not significantly change when 0.1 M KOH was added (Fig. 2). The λ_{max} of the dyes in methanol also showed hypsochromic shifts when 0.1 M HCl was added and absorption curves of the dyes resembled those in acetic acid (Fig. 2).

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

3.3. Substituent effects

As in apparent in Table 3, while introduction of electron-withdrawing chloro group into the ben-

Table 4
Absorption maxima (nm) of dyes **1**–**7** in acidic and basic solutions

Dye no.	DMSO	DMSO + piperidine	DMF	DMF + piperidine	Chloroform + piperidine	Methanol	Methanol + KOH	Methanol + HCl	Acetic acid
1	525, 455 s	535, 424 s	521, 452 s	532, 424 s	503, 430 s	515, 427 s	517, 429 s	411	406
2	540, 432 s	542, 423 s	538, 431 s	541, 425 s	504, 430 s	523, 430 s	526, 431 s	422	412
3	469, 444 s	470, 445 s	464, 440 s	468, 442 s	453, 435 s	427, 445 s	429, 446 s	414	411, 448 s
4	392, 471 s	396, 475 s	394, 472 s	394, 473 s	396, 472 s	383, 461 s	391, 470 s	360, 438 s	358, 439 s
5	384, 445 s	456, 393 s	383, 444 s	446, 389 s	378, 440 s	366, 430 s	351, 440 s	350, 410 s	350, 413 s
6	403, 501 s	503, 430 s, 541s	411, 502 s, 542s	423, 498 s, 541s	419, 494s, 541s	483, 398 s	502, 420 s	388	389
7	536	413, 533 s	528	415, 528 s	406, 504 s	498	502, 400 s	490	490

s: shoulder.

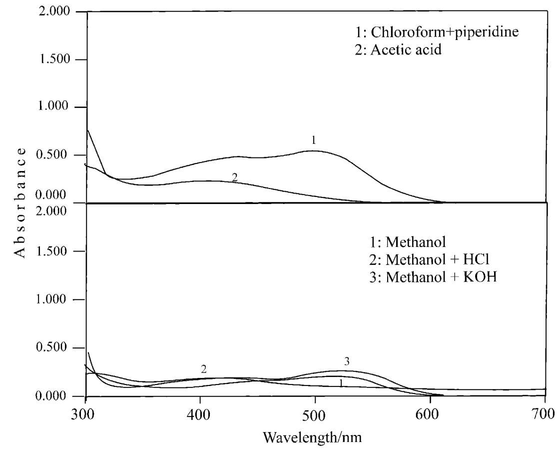


Fig. 2. Absorption spectra of dye **2** in acidic and basic solutions.

zothiazole ring resulted in bathochromic shifts in DMSO, DMF, methanol and acetic acid (for dye **2** $\Delta\lambda = 21$ nm relative to dye **1** for spectra in DMSO), but did not significantly change in acetonitrile and chloroform + piperidine. The introduction of electron-donating thiol group into the thiadiazole ring resulted in bathochromic shifts in DMSO, DMF, methanol, acetonitrile and acetic acid, but produced hypsochromic shift in chloroform + piperidine. The introduction of electron-donating thiol group into the thiadiazole ring stabilized the excited state one of the tautomeric forms, whereas dye **6** may exist between tautomeric forms and anionic form.

4. Conclusions

In this work, seven new Azocalix[6]arene have been synthesized from calix[6]arene and heterocyclic amines (2-aminobenzothiazole, 2-amino-6-chlorobenzothiazole, 2-aminobenzimidazole, 3-amino-5-methylmercapto-1,2,4-triazole, 3-amino-5-methylisoxazole, 2-amino-1,3,4-thiadiazole, 5-amino-1,3,4-thiadiazole-2-thiol) through a simple diazo-coupling reaction. These azocalix[6]arenes are higher yields and shows a lower melting points such as parents calix[6]arene. The characterization and absorption ability of hetarylazocalix[6]arene based dyes (**1**–**7**) was studied.

The results obtained show that all the absorption spectra are influenced by the forming azo-enol form and keto-hydrazo form species as well as solvent. This seems to confirm that dye **2** is an excellent compound for both acidic and basic solution media. In addition to the absorption ability of dye **1** is exhanced in various solvents.

In conclusion, it has been established that new molecular design azocalixarene ionophores, containing more than one diazo and hetarylazo cyclic unite, display versatile affinity for azo-enol and keto-hydrazo conformational forms.

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