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Dyes and Pigments 62 (2004) 141–148

DYES and PIGMENTS
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Azocalixarenes. 3: synthesis and investigation of the absorption spectra of hetarylazo disperse dyes derived from calix[4]arene

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Received 4 June 2003; received in revised form 8 October 2003; accepted 25 November 2003

Abstract

Synthesis of some novel hetarylazocalix[4]arene dyes was achieved by diazotisation of six heterocyclic amines using nitrosyl sulphuric acid, coupling with calix[4]arene. The absorption spectra of the dyes are discussed, both the effect of varying pH and solvent upon the absorption ability of azocalixarenes. The hetarylazocalix[4]arene readily undergo acidic dissociation into the common anion in DMF and DMSO. Absorption maxima of the dyes showed large bathochromic effects in comparison with analogues dyes containing carbocyclic amine residue. The colour of the 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; Azocalix[4]arenes; Heterocyclic amines; Calixarene dyes; Diazo-coupling reaction; Solvent effect; Substituent effect; Absorption properties

1. Introduction

Calix[4]arenes, the well-known family of macrocyclic compounds [1,2], frequently serve as molecular scaffolds for the construction of more elaborate supramolecular systems, such as various receptors possessing interesting complexation abilities towards target molecules or ions. It is known from the literature that the so-called *cone* conformation of calix[4]arene can interact with ammonium salts by cation–π interaction [3] between the aromatic part of the molecule (upper rim) and ammonium salts. The highest complexation constants in the solution were found in the cases where the *cone* conformation adopts the stable C_{4v} symmetry, which best the steric requirements of the interactions [4].

In recent years, efforts have been made to replace certain anthraquinone dyes with technically equivalent azo dyes, for both environmental and economic reasons [5]. In this regard, azo dyes based on heterocyclic amines have been developed, and the resultant dyes have been higher tinctorial strength and give brighter dyeings than those derived from aniline-based diazo components. For instance, amino-substituted thiazole, isothiazole, thiophene compounds afford very electronegative diazo components and, conse-

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doi:10.1016/j.dyepig.2003.11.015

quently, provide a pronounced bathochromic effect compared to the corresponding benzenoid compounds [6–8]. Moreover, it is well known that ring systems of this type are useful for providing blue and green azo dyes.

In contrast to the large number of investigations of the reactivity of carboaromatic diazonium ions in general and of the mechanism of their azo coupling reactions, very few comparable investigations have been made with heteroaromatic diazonium ions. Sawaguchi et al. [9] have measured the rate of azo coupling of various heteroaromatic diazonium ions with 2-naphthol-3,6-disulfonic acid. There exist an extensive patent literature on azo dyes synthesized with heteroaromatic diazonium ions since Dickey and Towne realized in the early 1950s, that industrially interesting disperse dyes can be obtained on this basis.

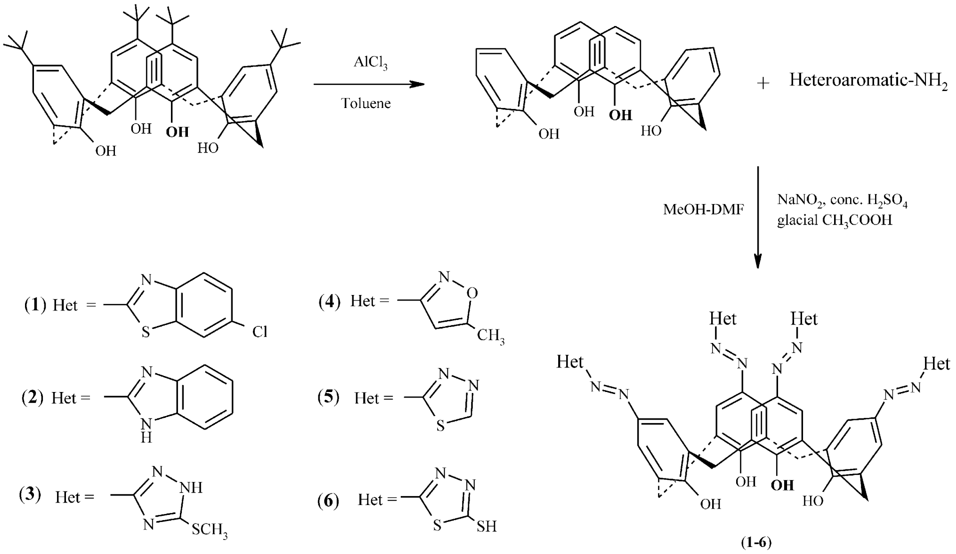
In the field of our investigations, we are interested in the development of a new class of chromogenic dyes. Azocalixarenes compounds containing calix[n]aren as coupling components have also been described as having from blue to violet various publications [10–12]. As a continuation of our previous work in this area [13,14], we report here in the synthesis of the calix[4]arenes **1–6** having calix[4]arene as the coupling component (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. ^{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 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.



Scheme 1. Hetarylazocalix[4]arene derivatives.

2.2. Preparation of the ligands

p-tert-Butylcalix[4]arene [15] and calix[4]arene [16] were synthesized as described by a previously reported method.

2.3. Preparation of hetarylazocalix[4]arene dyes (*1–6*)

Diazotisation of the various heterocyclic amines was effected with nitrosyl sulphuric acid. A typical procedure is that described below used for 2-amino-6-chlorobenzothiazole. *p*-(2-Benzimidazolylazo)calix[4]arene (**2**), *p*-(5-methylmercapto-1,2,4-triazol-3-ylazo)calix[4]arene (**3**), *p*-(5-methyl-3-isoxazolylazo)calix[4]arene (**4**), *p*-(1,3,4-thiadiazol-2-ylazo)calix[4]arene (**5**) and *p*-(1,3,4-thiadiazol-2-thiol-5-ylazo)-calix[4]arene (**6**) were obtained using the same method in 61–83% 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-(6-chloro-2-benzothiazolylazo)calix[4]arene (*1*)

2-Amino-6-chlorobenzothiazole (1.85 g, 10 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 from sodium nitrite (0.69 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[4]arene (1 g, 2.36 mmol) in DMF–H_2O (26 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: 63%, m.p: dec. 250 °C).

3. Results and discussion

3.1. Synthesis and characterizations

The hetarylazocalix[4]arene dyes **1**–**6** were prepared by coupling calix[4]arene with diazotized heterocyclic amines in nitrosyl sulphuric acid

Table 1
Spectral data for hetarylazocalix[4]arene dyes **1–6**

Dye no.	FT-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	3320	3089 3027	2928	1679	1589	1107	7.22–8.16 (20H, m)	2.25 and 4.17 (8H, s)	11.23 (OH, b) 14.82 (NH, b)	DMSO-d_6
2	3280	3089 3036	2946	1705	1625	1089	7.21–7.75 (24H, m)	2.15 and 4.20 (8H, s)	9.61 (4H, b) 11.56 (OH, b) 14.72 (NH, b)	DMSO-d_6
3	3310	3080 3000	2929	1661	1589	1125	7.22–7.60 (8H, m)	2.90 (12H, s) 2.23 and 4.19 (8H, s)	12.17 (4H, b) 10.81 (OH, b) 14.27 (NH, b)	DMSO-d_6
4	3310	3100	2928	1688	1607	1116	6.10–7.87 (12H, m)	2.45 (12H, s) 2.18 and 4.17 (8H, s)	11.81 (OH, b) 14.18 (NH, b)	DMSO-d_6
5	3290	3071 3018	2946	1679	1589	1107	7.22–9.69 (12H, m)	2.25 and 4.17 (8H, s)	10.42 (OH, b) 13.71 (NH, b)	DMSO-d_6
6	3280	3089 3036	2946	1696	1607	1116	7.22–7.61 (8H, m)	2.09 and 4.18 (8H, s)	2.37 (4H, SH, b) 10.37 (OH, b) 13.68 (NH, b)	DMSO-d_6

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

Table 2
Element analysis of hetarylazocalix[4]arene dyes **1–6**

Dye no.	Molecular formula	Molecular mass	Yield %	C %		H %		N %		S %		Melting point °C
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
1	$C_{56}H_{32}Cl_4N_{12}O_4S_4$	1206	63	55.72	56.12	2.65	2.73	13.93	13.37	10.61	10.28	dec. > 250
2	$C_{56}H_{40}N_{16}O_4$	1000	83	67.20	67.42	4.00	4.11	22.40	21.98	–	–	dec. > 250
3	$C_{40}H_{36}N_{20}O_4S_4$	988	61	48.58	48.81	3.64	3.72	28.34	27.87	12.96	12.44	dec. > 250
4	$C_{44}H_{36}N_{12}O_8$	860	73	61.39	61.65	4.19	4.22	19.53	19.15	–	–	dec. > 200
5	$C_{36}H_{24}N_{16}O_4S_4$	872	64	49.54	49.71	2.75	2.88	25.69	25.43	14.69	14.43	dec. > 250
6	$C_{36}H_{24}N_{16}O_4S_8$	1000	61	43.20	43.46	2.40	2.54	22.40	21.87	25.60	25.06	dec. > 300

(Scheme 1). The effect of the nature of substituents on the colour of the azocalix[4]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 hetarylazocalix[4]arene derivatives are reported. No details of the synthesis and wavelength shift behaviour of such compounds have been published hitherto.

Herein, we report the synthesis of six new hetarylazocalix[4]arenes moieties. At first *p*-*tert*-butylcalix[4]arene was prepared by reaction of *p*-*tert*-butylphenol with formaldehyde according to the method of Gutsche [15]. Treatment of *p*-*tert*-butylcalix[4]arene with aluminium chloride gave calix[4]arene according to the method described by Gutsche et al. [16]. Then we synthesized the heterocyclic diazonium salt derivatives from heterocyclic amines in nitrosyl sulphuric acid, after then we employed 4 equivalent of these salts in 5:8 MeOH:DMF mixture with 1 equivalent of calix[4]arene to obtain the corresponding hetarylazocalix[4]arenes **1**–**6**. This general reaction described in Scheme 1.

The diazonium salts were an excellent electrophiles and would attack any available position on the calix[n]arenes to yield complex mixture. Work up of the reaction mixtures afforded the corresponding six hetarylazocalix[4]arenes in 61–83% yield.

The above reaction products were characterized using elemental analysis, FT-IR and ^{1}H-NMR spectral data. The hetarylazocalix[4]arenes (**1**–**6**) may exist in two possible tautomeric forms, namely an azo-enol form A and keto-hydrazo form B. Deprotonation of two tautomers lead to common anions. The FT-IR spectra of all compounds (**1–6**) showed a weak band within the range 3320–3280 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 3100–3000 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 1607–1589 cm^{-1} was masked by the intense bands due to ring vibration. The other ν_{max} values of 2946-2928 cm^{-1} (aliphatic C–H), 1705–1661 cm^{-1} (C=C), 1125–1089 cm^{-1} (C–O) were recorded. The infrared spectra of all compounds (in KBr) showed broad –OH bands at 3100–3000 cm^{-1}. It can be suggested that these compounds do not exist as the keto-hydrazo form in the solid state.

The structures of **1–6** 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 4.17–4.20, a singlet at 2.90 (–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 10.37–11.81 (–OH), a broad peak at 13.68–14.82 (–NH), a broad peak at 9.61 (–NH), a broad peak at 12.17 (–NH) and a broad peak at 2.37 (–SH). At room temperature the singlets at 10.37–11.81 and 13.68–14.82 indicate that the compounds may be exist a mixture of several tautomeric forms in DMSO-d_6.

The present paper describe for the first time the synthesis of calix[4]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 hetarylazocalix[4]arene dyes **1–6** were recorded in various solvents at a concentration of $\sim 10^{-6}$–10^{-8} M and these are all run at different concentrations. The results were 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 a strong solvent dependency which did not show regular variation with the polarity of solvents.

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 **5** in different solvents (Fig. 1). This equilibrium may exist between tautomeric forms. But, compound **1** showed three absorption peaks in DMF and compound **5** showed three absorption peaks in chloroform + piperidine. The equilibrium of compound **1** in DMF and compound **5** in chloroform + piperidine may exist between tautomeric forms and anionic forms (Scheme 2). Absorption peaks at the longest wavelength of compound **1** and compound **5** may a peak of anionic forms. This indicates that compound **1** exist in dissociated in DMF and compound **5** exist in a dissociated in chloroform + piperidine. The equilibrium depends on the basicity of the solvent used; in proton accepting solvents such as DMSO, DMF, chloroform + piperidine, acetonitrile and methanol, displayed a red shift of the λ_{max} respect to the absorption spectra in acetic acid (e.g. for compound **3** λ_{max} is 349 nm in acetic acid, 388 nm in DMSO and 397 nm in DMF, for compound **5** is 383 nm in acetic acid, 496 nm in DMSO and 498 nm in DMF).

Table 3
Influence of solvent on λ_{max} (nm) of hetarylazocalix[4]arene dyes **1–6**

Dye no.	DMSO		DMF		Chloroform + piperidine		Methanol		Acetonitrile		Acetic acid	
	Conc.	Dil.	Conc.	Dil.	Conc.	Dil.	Conc.	Dil.	Conc.	Dil.	Conc.	Dil.
1	424, 520 s	420, 520 s	546, 422 s, 495 s	546, 422 s, 495 s	420, 513 s	419, 498 s	424, 508 s	426, 506 s	509, 414 s	509, 415 s	312, 408 s	312, 407 s
2	420, 457 s	431, 457 s	464, 435 s	466, 436 s	457, 433 s	455, 432 s	425, 459 s	426, 459 s	471	466	413, 550 s	414, 551 s
3	388, 463 s	389, 463 s	397, 470 s	397, 470 s	390, 462 s	386, 460 s	–	–	-	–	349	348
4	371, 442 s	369, 442 s	371, 442 s	371, 442 s	361, 424 s	359, 422 s	331, 423 s	336, 423 s	343, 417 s	344, 418 s	336	336
5	496, 427 s	498, 425 s	498, 433 s	498, 433 s	496, 429 s, 552 s	491, 423 s, 560 s	409, 478 s	409, 477 s	399, 482 s	402, 483 s	383	383
6	428, 529 s	429, 530 s	527, 420 s	527, 420 s	506, 424 s	506, 423 s	500, 420 s	502, 419 s	413, 509 s	415, 510 s	412	412

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

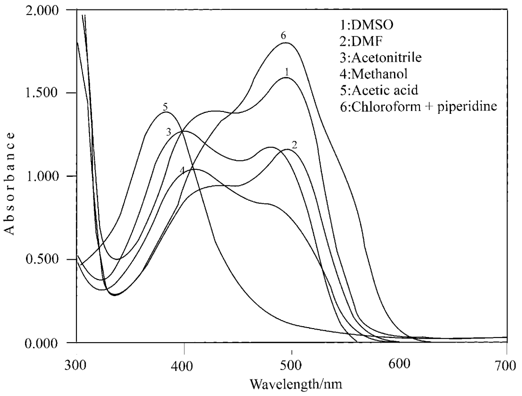


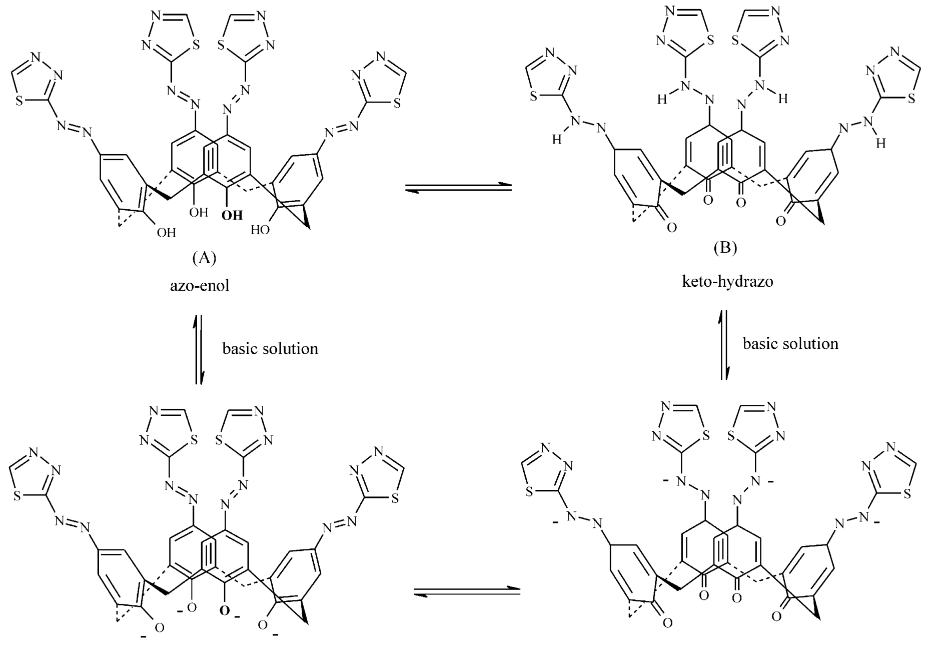
Fig. 1. Absorption spectra of dye **5** in various solvents.

Heterocyclic based azo disperse dyes tend to show larger solvatochromic effects than azobenzenes because of the increased polarity of the dye system, especially of the excited state. Similar effects for dyes containing a benzothiazolyl, thiazolyl thienyl moieties have been reported for some derivatives of *N*-β-cyanoethyl-*N*-β-hydroxyethyl aniline [17–21].

The λ_{max} of compound **1** and compound **5** showed bathochromic effects when a small amount of piperidine was added to their solutions in DMSO. The λ_{max} of compound **5** also showed bathochromic effect when a small amount of piperidine was added to its solution in DMF. The λ_{max} values of dyes **2**, **3**, **4** and **6** did not change significantly when a small amount of piperidine was added to their solutions in DMSO or DMF (Table 4).

The λ_{max} of compound **1** and compound **5** in methanol also showed bathochromic effects when 0.1 M KOH was added. This findings indicates that compound **1** and compound **5** exist in the anionic form in DMSO + piperidine, DMF + piperidine and methanol + KOH (Fig. 2). The λ_{max} of the compounds in methanol also showed hypsochromic effects when 0.1 M HCl was added with the exception of compound **3** and compound **4** (Table 4).

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



Scheme 2. The tautomeric forms and anionic forms of 4-(thiadiazolylazo)calix[4]arene (**5**).

Table 4
Absorption maxima (nm) of hetarylazocalix[4]arene dyes **1–6** in acidic and basic solvents

Dye no.	DMSO	DMSO + piperidine	DMF	DMF + piperidine	Chloroform + piperidine	Methanol	Methanol + KOH	Methanol + HCl	Acetic acid
1	420, 520 s	558, 428 s, 497 s	546, 422 s, 495 s	550, 425 s, 500 s	419, 498 s	426, 506 s	526, 421 s	315, 412 s	312, 407 s
2	431, 457 s	475, 429 s	466, 436 s	469, 438 s	455, 432 s	426, 459 s	430, 461 s	414, 556 s	414, 551 s
3	389, 463 s	397, 470 s	397, 470 s	393, 470 s	386, 460 s	–	391	–	348
4	369, 442 s	450, 376 s	371, 442 s	444, 380 s	359, 422 s	336, 423 s	429, 366 s	345	336
5	498, 425 s	509, 441s, 478 s, 549 s	498, 433 s	508, 440 s, 478 s, 550 s	491, 423 s, 560 s	409, 477 s	547, 457 s, 517 s	385	383
6	429, 530 s	534, 424 s	527, 420 s	528, 422 s	506, 423 s	502, 419 s	422, 509 s	427	412

s: shoulder.

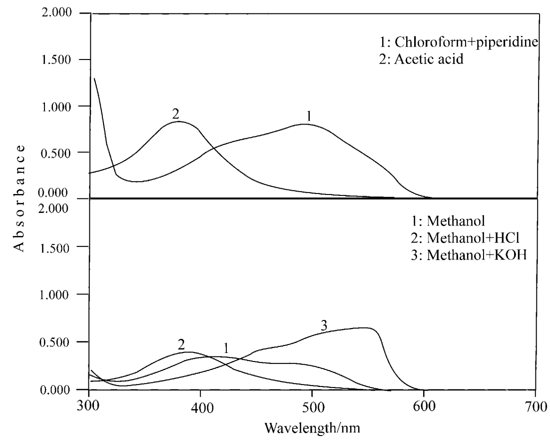


Fig. 2. Absorption spectra of dye **5** in acidic and basic solutions.

3.3. Substituent effects

The UV spectra of dyes **1–6** generally show two absorption bands in the region 300–700 nm. The relatively small difference in the $\lambda_{\max}$ may be caused by the polarity change of the absorbing system caused by solvent interactions due to the general solvent effect. However, the UV spectra of dye **1** and dye **5** show three absorption bands in DMSO and chloroform + piperidine, respectively. These results indicate that dye **1** and dye **5** were found state of common anions forms in DMSO and chloroform + piperidine, respectively. Similar effects are apparent in substituted phenylazocalix[6]arenes [14].

As in apparent in Table 3, the introduction of electron-donating thiol group into the thiadiazole ring resulted in bathochromic shifts in DMF, chloroform + piperidine, acetic acid, acetonitrile and methanol (for dye **6** $\Delta\lambda = 29$ nm relative to dye **5** for spectra in DMF).

4. Conclusions

In summary, the synthesis, characterization and absorption ability of six novel hetarylazocalix[4]arene based dyes (**1–6**) was studied. The absorption spectra results of their the dyes (**1–6**) revealed that these compounds do exist in forming azo-enol form and keto-hydrazo form species. The conformational studies show that dye **5** is an excellent compound for both acidic and basic solution media. Moreover, the absorption ability of dye **5** is enhanced in various solvents.

It has been suggested that, by the introduction of diazo functions and/or bridges or by choosing a particular conformation, the azocalixarene based receptors could be proved to find remarkable applications in the design of chemical sensors, using an electrochemical transduction, as conventional ion-selective electrodes (ISE) and micro contact printing (μCP) with heavyweight inks.

Acknowledgements

The authors are grateful to TÜBİTAK for financial support the project number of TBAG-AY/273.

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