

# The synthesis and characterization of calix[4]arene based azo dyes

Shobhana K. Menon · Ravindra V. Patel ·  
Jayesh G. Panchal

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**Abstract** A series of azocalix[4]arene dyes (1–7) were prepared by linking 2,4-di-chloroaniline, 2,4,5-tri-chloroaniline, 2,4-di-nitroaniline, 2-nitro *p*-toluidin, 4-nitro *o*-toluidin, 5-nitro *o*-toluidin and sulfanilic acid, to calix[4]arene through a diazo-coupling reaction. These compounds were characterized by elemental analysis, FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, MALDI-TOF, UV-Vis., DSC, and DTA. The absorption properties of the synthesized dyes were studied and the application of the water soluble dye on cotton and wool was discussed. Solvent based inks were investigated and the fastness properties of formulated inks were also discussed.

**Keywords** Calix[4]arene dyes · Spectral properties · Application on cotton and wool · Fastness studies · Ink formulation

## Introduction

Calixarenes have been widely used as three dimensional building blocks for the construction of artificial molecular receptors capable of recognizing neutral molecules, cations and anions [1–5]. They have effective binding properties for a particular set of cation and anions. Chromogenic cone calix[4]dibenzothiacrown ethers containing nitrophenylazo groups have been used for their cation binding ability for the transition metal ions [6]. Chromogenic azocalix[4]arene was reported for application as liquid crystal [7] an also as ionic and NLO sensors [8], however most of

these studies were restricted to the investigation of absorption spectra of the azocalixarenes. There are few reports in which macrocyclic calixarenes have been used as components for the preparation of azo dyes. Calixarenes were frequently reported as the coupling component for various diazotized aromatic amines [9–12]. The attachment of calixarene unit to the chromophores will increase the molecular weight of the dyes since the bulky organic groups acts as “ballast group” and this has been our strategy in preparing calixarene dyes. This also will enhance the tinctorial value, solubility and stability. In earlier report [13] crown ether based disazo dyes were investigated for application as active coloring agents in solvent based inks. Since work has been reported so far on the application of azocalix[*n*]arenes as active colouring agents, it was proposed to synthesize and study the application of azocalixarene.

Thus, the chromogenic compounds reported here were designed to take advantage of the first series of calixarene dyes which are to be used as active coloring agents. The properties of the synthesized dyes and their applications as active coloring agents in solvent based inks, cotton, wool and their suitability for the textile industry were investigated extensively.

## Experimental

### General

Compounds 2,4-di-chloroaniline, 2,4,5-tri-chloroaniline, 2,4-di-nitroaniline, 2-nitro *p*-toluidin, 4-nitro *o*-toluidin, 5-nitro *o*-toluidin and sulfanilic acid derivatives were obtained as gift samples from Anar chemical, Ahmedabad and were purified before use. All other chemicals and

S. K. Menon (✉) · R. V. Patel · J. G. Panchal  
Department of Chemistry, School of Sciences, Gujarat  
University, Ahmedabad 380009, India  
e-mail: shobhanamenon07@gmail.com

solvents used were of analytical grade and were used without further purification. Melting points were obtained from DTA thermogram. The FT-IR spectra were recorded as KBr pellet on Bruker TENSOR-27. Discover Bench-Mate system-240V (CEM Corporation) microwave synthesizer is used for synthesis. The MALDI-TOF MS was run on a Micromass TofSpec 2E instrument, using a nitrogen 337 nm laser (4 ns pulse).  $^1\text{H}$  NMR spectra were scanned on 400 MHz FT-NMR Bruker Avance-400 and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX-400 spectrometer with tetramethylsilane (TMS) as internal standard in deuterated DMSO.

The ink formulations were prepared using a Marshal MV614 vibroshaker. The resultant formulations were applied to polyester films, aluminium foils, coated as well as uncoated paper manually using a barcoater no. 2.

#### Preparation of the ligands

*p*-tert-Butylcalix[4]arene was synthesized by microwave technique developed in our laboratory [11] and the debutylation of calix[4]arene was carried out by the reported method [14].

#### Preparation of phenylazocalix[4]arene dyes ( $\mathbf{d}_1$ – $\mathbf{d}_7$ )

The diazotisation of the various amines was effected with sodium nitrite and HCl. A typical procedure is that described below which is used for the synthesis of 2,4-dichloroaniline. *p*-(2,4,5-tri-chlorophenylazo) calix[4]arene ( $\mathbf{d}_2$ ), *p*-(2,4-di-nitrophenylazo) calix[4]arene ( $\mathbf{d}_3$ ), *p*-(2-nitro, 4-methylphenylazo) calix[4]arene ( $\mathbf{d}_4$ ), *p*-(4-nitro, 2-methylphenylazo) calix[4]arene ( $\mathbf{d}_5$ ), *p*-(5-nitro, 2-methylphenylazo) calix[4]arene ( $\mathbf{d}_6$ ) and *p*-(sulfophenylazo) calix[4]arene ( $\mathbf{d}_7$ ) were obtained using the same method in 58–91% yield. The compounds obtained were purified by crystallization using the same solvent (DMF–methanol) and were then analyzed.

#### Synthesis of *p*-(2,4-di-chlorophenylazo) calix[4]arene ( $\mathbf{d}_1$ )

A solution of 2,4-di-chlorophenyldiazonium chloride, which was prepared from 2,4-chloroaniline (7.84 g, 40 mmol), sodium nitrite (1.69 g, 25 mmol) and conc. HCl (7 mL) in water (25 mL), was added slowly to a cold (0–5 °C) solution of calix[4]arene (4.25 g, 10 mmol) and sodium acetate trihydrate (4.08 g, 30 mmol) in DMF–methanol (26 mL, 8:5, 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 (yield, 1.67 g, 72%) a dark yellow solid,

which was filtered and washed with water and methanol. A sample for analysis was obtained as follows:  $\mathbf{d}_1$  was dissolved in 100 mL of hot aqueous  $\text{NaHCO}_3$  (4.2 g) solution; to this solution was added activated charcoal (1 g). After the charcoal was filtered, the filtrate was cooled to 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/methanol mixture gave a dark yellow product. The compound is soluble in DMSO, DMF, chloroform, methanol and slightly soluble in acetone. Yield, 1.95 g (85%), mp dec. > 230 °C. Anal. calc.  $\text{C}_{52}\text{H}_{32}\text{N}_8\text{Cl}_8\text{O}_4$ : C: 55.94; H: 4.92; N: 10.04% Found: C: 55.68; H: 4.42; N: 10.47%. **FT-IR** (KBr)  $\nu$ : 3340  $\text{cm}^{-1}$  (–OH), 2950, 1485  $\text{cm}^{-1}$  (N=N).  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ )  $\delta$  9.82 (s, 4H, Ar OH), 7.5 (s, 12H, Ar H), 2.69 (s, 8H,  $\text{CH}_2$ ), 7.80 (s, 8H, Ar H).  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ )  $\delta$  162, 151, 145, 140, 135, 130, 129, 128, 124, 118 and 113 (ArC), 13.0 (– $\text{CH}_2$ –). **MALDI-TOF MS** ( $m/z$ ) 1,116 (M) 1,117 (M + 1).

#### *p*-(2,4,5-tri-chlorophenylazo) calix[4]arene ( $\mathbf{d}_2$ )

The dye  $\mathbf{d}_2$  was prepared as described above, recrystallization from DMF/methanol mixture gave a dark yellow product. The compound is soluble in DMSO, DMF, chloroform, methanol and slightly soluble in acetone. Yield, 1.40 g (72%), mp dec. > 211 °C. Anal. calc.  $\text{C}_{52}\text{H}_{28}\text{N}_8\text{Cl}_{12}\text{O}_4$ : C: 49.79; H: 2.25; N: 8.93% Found: C: 50.20; H: 2.05; N: 8.67%. **FT-IR** (KBr)  $\nu$ : 3339  $\text{cm}^{-1}$  (–OH), 2950, 1490  $\text{cm}^{-1}$  (N=N).  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ )  $\delta$  9.82 (s, 4H, Ar OH), 7.25 (s, 8H, Ar H), 2.69 (s, 8H,  $\text{CH}_2$ ), 7.80 (s, 8H, Ar H).  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ )  $\delta$  161, 158, 147, 139, 133, 131, 130, 128, 125, 119 and 115 (ArC), 13.0 (– $\text{CH}_2$ –). **MALDI-TOF MS** ( $m/z$ ) 1,254 (M).

#### *p*-(2,4-di-nitrophenylazo) calix[4]arene ( $\mathbf{d}_3$ )

The synthesis of dye  $\mathbf{d}_3$  is as described above and the, recrystallization from DMF/methanol mixture gave a dark brown product. The compound is soluble in most of the organic solvents. Yield, 1.44 g (80%), mp dec. > 245 °C. Anal. calc.  $\text{C}_{52}\text{H}_{32}\text{N}_{16}\text{O}_{20}$ : C: 49.79; H: 2.25; N: 8.93% Found: C: 50.20; H: 2.05; N: 8.67%. **FT-IR** (KBr)  $\nu$ : 3245  $\text{cm}^{-1}$  (–OH), 2950, 1480  $\text{cm}^{-1}$  (N=N).  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ )  $\delta$  9.82 (s, 4H, Ar OH), 8.5 (s, 12H, Ar H), 2.69 (s, 8H,  $\text{CH}_2$ ), 7.60 (s, 8H, Ar H).  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ )  $\delta$  160, 155, 148, 144, 139, 135, 131, 128, 122, 119 and 118 (ArC), 13.0 (– $\text{CH}_2$ –). **MALDI-TOF MS** ( $m/z$ ) 1,201 (M) 1,202 (M + 1).

#### *p*-(2-nitro, 4-methylphenylazo) calix[4]arene ( $\mathbf{d}_4$ )

The dye,  $\mathbf{d}_4$ , prepared by following the above method was above, recrystallized from DMF/methanol mixture gave a

orange product. The compound is soluble in DMSO, DMF, chloroform, methanol and slightly soluble in acetone. Yield, 1.44 g (78%), mp dec. > 235 °C. Anal. calc.  $C_{56}H_{44}N_{12}O_{12}$ : C: 62.45; H: 4.12; N: 15.61% Found: C: 62.50; H: 4.02; N: 15.66%. **FT-IR** (KBr)  $\nu$ : 3255  $cm^{-1}$  (–OH), 2950, 1489  $cm^{-1}$  (N=N).  **$^1H$  NMR** ( $CDCl_3$ )  $\delta$  9.80 (s, 4H, Ar OH), 8.32 (s, 8H, Ar H), 2.69 (s, 8H,  $CH_2$ ), 7.68 (s, 12H, Ar H), 2.30 (d, 12H,  $-CH_3$ ).  **$^{13}C$  NMR** ( $CDCl_3$ )  $\delta$  161, 151, 145, 143, 141, 135, 128, 125, 120, 118 and 115 (ArC), 13.0 ( $-CH_2-$ ), and 20 ( $-CH_3$ ). **MALDI-TOF MS** ( $m/z$ ) 1,078 (M + 1).

#### *p*-(4-nitro, 2-methylphenylazo) calix[4]arene (*d*<sub>5</sub>)

*d*<sub>5</sub> is prepared as described above, recrystallization from DMF/methanol mixture gave a dark orange product. The compound is soluble in DMSO, DMF, chloroform, methanol and slightly soluble in acetone. Yield, 1.38 g (70%), mp dec. > 220 °C. Anal. calc.  $C_{56}H_{44}N_{12}O_{12}$ : C: 63.15; H: 4.02; N: 13.31% Found: C: 63.55; H: 4.32; N: 13.26%. **FT-IR** (KBr)  $\nu$ : 3255  $cm^{-1}$  (–OH), 2950, 1487  $cm^{-1}$  (N=N).  **$^1H$  NMR** ( $CDCl_3$ )  $\delta$  9.82 (s, 4H, Ar OH), 8.22 (s, 8H, Ar H), 2.69 (s, 8H,  $CH_2$ ), 7.60 (s, 12H, Ar H), 2.76 (d, 12H,  $-CH_3$ ).  **$^{13}C$  NMR** ( $CDCl_3$ )  $\delta$  161, 154, 150, 145, 141, 135, 128, 125, 120, 117 and 113 (ArC), 13.0 ( $-CH_2-$ ), and 16.8 ( $-CH_3$ ). **MALDI-TOF MS** ( $m/z$ ) 1,078 (M + 1).

#### *p*-(5-nitro, 2-methylphenylazo) calix[4]arene (*d*<sub>6</sub>)

*d*<sub>6</sub> is prepared as described above, recrystallization from DMF/methanol mixture gave a pale orange product. The compound is soluble in DMSO, DMF, chloroform, methanol and slightly soluble in acetone. Yield, 1.48 g (78%), mp dec. > 225 °C. Anal. calc.  $C_{56}H_{44}N_{12}O_{12}$ : C: 62.35; H: 3.72; N: 11.51% Found: C: 62.55; H: 3.32; N: 11.86%. **FT-IR** (KBr)  $\nu$ : 3255  $cm^{-1}$  (–OH), 2950, 1487  $cm^{-1}$  (N=N).  **$^1H$  NMR** ( $CDCl_3$ )  $\delta$  9.85 (s, 4H, Ar OH), 8.11 (s, 8H, Ar H), 2.69 (s, 8H,  $CH_2$ ), 7.60 (s, 12H, Ar H), 2.76 (d, 12H,  $-CH_3$ ).  **$^{13}C$  NMR** ( $CDCl_3$ )  $\delta$  161, 154, 150, 145, 141, 135, 128, 125, 120, 117 and 113 (ArC), 13.0 ( $-CH_2-$ ), and 17.18 ( $-CH_3$ ). **MALDI-TOF MS** ( $m/z$ ) 1,078 (M + 1).

#### Synthesis of *p*-(sulfo-phenylazo) calix[4]arene (*d*<sub>7</sub>)

*d*<sub>7</sub> was prepared as described above, recrystallization from DMF/methanol mixture gave a dark orange product. The compound is soluble in water, DMSO, DMF, methanol and slightly soluble in acetone. yield, 1.44 g (58%), mp dec. > 230 °C. Anal. calc. For  $C_{52}H_{40}N_8O_{16}S_4$ : C: 53.79; H: 3.74; N: 9.65% Found: C: 53.50; H: 3.80; N: 9.88%. **FT-IR** (KBr)  $\nu$ : 3223  $cm^{-1}$  (–OH), 2950, 1484  $cm^{-1}$  (N=N).  **$^1H$  NMR** ( $CDCl_3$ )  $\delta$  9.75 (s, 4H, Ar OH), 8.20 (s, 16H, Ar H), 2.69 (s, 8H,  $CH_2$ ), 7.4 (s, 8H, Ar H), 2.0 (d, 4H, Alip).

**$^{13}C$  NMR** ( $CDCl_3$ )  $\delta$  161, 154, 150, 135, 131, 129, 128, 123, 120, 117 and 113 (ArC), and 13.0 ( $-CH_2-$ ). **MALDI-TOF MS** ( $m/z$ ) 1,162 (M + 1).

#### Preparation of inks

The synthesized dyes were used for formulating solvent based inks as reported earlier [15]. To a mixture of 6 g dye, 25 g resin (maleic resin for paper, acrylic resin for polyester film and nitrocellulose resin for aluminium foil) and 60 g of appropriate solvent (ethanol for paper, ethyl acetate for polyester films, glycol ether and ethyl acetate mixture for aluminium foils) in a vibroshaker container was added 80 g glass beads and the mixture was shaken for 20 min.

The inks were then transferred to their corresponding substrates manually using a barcoater rod no. 2, and then allowed to dry for 3–5 min at 35 °C. The light and wet fastness studies were done according to standard method [16, 17].

#### Dyeing of cotton

The water soluble dye *d*<sub>7</sub> (0.30 g) was added to water (25 mL) and heated to 60 °C. The scoured cotton hanks (3.0 g) were added to the dye baths and dyed at 90 °C for about 1 h. After cooling the baths to room temperature the dyed hanks were rinsed with cold water and dried.

#### General procedure for spectral studies and ionization constants ( $pK_a$ )

For spectral studies  $10^{-4}$ – $10^{-5}$  M dye solutions in various solvents were used and the effect of acid and base was studied by addition of 50% acetic acid and 0.1 M sodium hydroxide respectively.

For  $pK_a$  measurements,  $10^{-4}$ – $10^{-5}$  M dye solutions in DMSO in the pH range of 2–13 were made and the spectra were recorded at 25 °C in the range of 300–650 nm. The ionization constants were then calculated using the following equation:

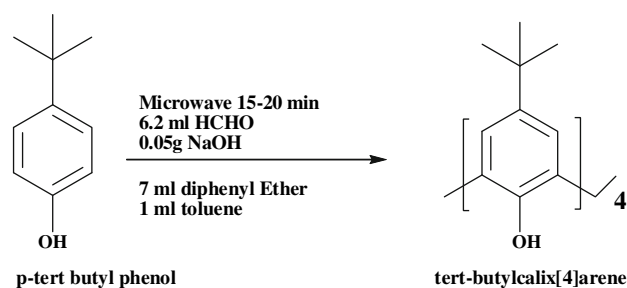
$$pK_a = pH + \log_{10} \frac{A - A_b}{A_a - A}$$

where A is the absorbance at the specific pH,  $A_a$  and  $A_b$  are the absorbances for the most acidic and most basic pH, respectively [18].

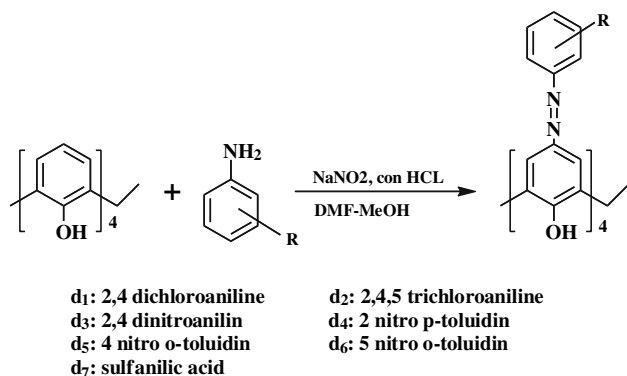
## Results and discussion

### Synthesis and characterizations

Microwave synthesis of calix[4]arene was carried out (Scheme 1) for the first time by base-catalysed



**Scheme 1** Microwave-assisted synthesis of *tert*-butyl calix[4]arene



**Scheme 2** Synthesis scheme of *o*-, *m*- and *p*-substituted azocalix[4]arene derivatives

condensation of *p*-substituted phenol and formaldehyde with an improvement of yield to 90–95% [7]. Microwave synthesis of the parent molecule is adopted to reduce the cost of the final product. The calix[4]arene macrocycle in its cone conformation is a very versatile molecule. In this work, seven azo compounds were synthesized from 2,4-dichloroaniline, 2,4,5-trichloroaniline, 2,4-di-nitroaniline, 2-nitro *p*-toluidin, 4-nitro *o*-toluidin, 5-nitro *o*-toluidin and sulfanilic acid. These compounds (d<sub>1</sub>–d<sub>7</sub>) are shown in Scheme 2. The synthesized azocalix[4]arene compounds were characterized using elemental analysis, FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and MALDI-TOF MS.

The FT-IR spectra of all compounds (d<sub>1</sub>–d<sub>7</sub>) showed a band within the range 3,339–3,212 cm<sup>-1</sup> corresponding to ν OH. Asymmetrical stretching vibration of the N=N group leading to the band located in the 1,478–1,490 cm<sup>-1</sup> region. The compounds (d<sub>1</sub>–d<sub>7</sub>) were examined in solution by high-resolution NMR. The <sup>1</sup>H NMR spectrum showed broad peak at δ = 9.75–9.82 ppm (–OH), singlet peak for methylene bridge protons (–CH<sub>2</sub>–) at δ = 2.4–2.76 ppm, singlet from δ = 7.20 to 9.12 ppm for aromatic protons (Aro-H), doublet from δ = 2.0 to 2.76 ppm for aliphatic protons (Alip-H). The <sup>13</sup>C NMR spectrum showed aromatic (ArC) at δ = 112.3–170.1 ppm, methylene bridge carbon showed peak at δ = 13.0 ppm, (–CH<sub>3</sub>) at δ = 17.19–20.4 ppm.

## Thermal properties

The decomposition temperatures were taken from the DSC curves of the dyes. The temperature at which the dyes first exothermic peak starts appearing after the melting point was taken as the decomposition temperature. The melting points and decomposition temperatures of all the synthesized dyes are as shown in Table 1. All prepared dyes showed high melting points (mp 211–251 °C) and consequently high thermal stability.

## Proton ionization constants

The ionization constants are a core property of a molecule which reflects its structural characteristics, reactivity, spectral properties and the isolation conditions. All the measurements were done in DMSO medium. From the values of the ionization constants summarized in Table 2 it can be easily concluded that dye d<sub>3</sub> is the most acidic in nature. This implies directly that of all the dyes synthesized, dye d<sub>3</sub> has more tendencies to be taken up in an aqueous solution than into organic solvents. Hence it will have comparatively less solvent solubility and water fastness than the other dyes.

## Absorption spectra

The spectral details of the synthesized calix[4]arene dyes are summarized in Table 2. The dyes showed colors ranging from deep red (λ<sub>max</sub> 521 nm) to pale yellow (λ<sub>max</sub> 340 nm). The different substituents are in positions slightly away from the chromophoric systems. Hence they may not directly influence the absorption maxima. But the general observation made is that most of the substituted dyes have higher absorption maxima when compared to their unsubstituted analogues.

The molar extinction coefficient (ε<sub>max</sub>) of the dyes showed that most of them are intensely absorbing. However, it is the oscillator strength (*f*) that gives a full measure of the tinctorial strength rather than molar extinction coefficient (ε<sub>max</sub>) [19, 20]. Hence, the oscillator strength was calculated using the following equation:

**Table 1** Thermal properties of dyes d<sub>1</sub>–d<sub>7</sub>

Dye	Melting point (Decom temp)°C
d <sub>1</sub>	230 (>250)
d <sub>2</sub>	211 (>250)
d <sub>3</sub>	245 (>280)
d <sub>4</sub>	235 (>250)
d <sub>5</sub>	220 (>250)
d <sub>6</sub>	225 (>250)
d <sub>7</sub>	245 (>280)

**Table 2** Oscillator strength for the dyes d<sub>1</sub>–d<sub>7</sub>

Dyes	$\lambda_{\max}$ (nm)	$\Delta\nu_{1/2}$ (cm <sup>-1</sup> )	$\epsilon_{\max}$ (mol <sup>-1</sup> cm <sup>-1</sup> )	$f$	Ionization constants
d <sub>1</sub>	501	6,218	55,235	1.48370	11.71
d <sub>2</sub>	475	5,513	50,516	1.20309	11.39
d <sub>3</sub>	411	5,488	49,786	1.86342	06.54
d <sub>4</sub>	479	5,515	52,234	1.24449	08.21
d <sub>5</sub>	468	5,514	51,965	1.23783	08.93
d <sub>6</sub>	409	5,467	49,543	1.17007	07.16
d <sub>7</sub>	521	6,220	57,342	1.54080	08.80

$$f = 4.23 \times 10^{-9} \times \Delta\nu_{1/2} \times \epsilon_{\max}$$

where  $f$  is Oscillator strength,  $\epsilon_{\max}$  is the molar extinction coefficient at maximum absorption,  $\Delta\nu$  is the full width at half maximum of the absorption curves for the dyes.

#### Solvatochromic effects

The absorption spectra of azocalix[4]arenes d<sub>1</sub>–d<sub>7</sub> were recorded in various solvents at a concentration of  $1 \times 10^{-4}$ – $1 \times 10^{-5}$  M; the results are summarized in Table 3. The electronic absorption spectra of azocalix[4]arene derivatives (d<sub>1</sub>–d<sub>7</sub>) exhibited one absorption band in the range 300–700 nm corresponding to  $\pi$ – $\pi^*$  and  $n$ – $\pi^*$  transitions. 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 visible absorption spectra of the compounds were found to exhibit strong 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 equilibrium is provided by the isosbestic points in the visible spectra of, for example, compound d<sub>3</sub> in different solvents. 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, chloroform

**Table 3** Influence of solvent on  $\lambda_{\max}$  (nm) dyes d<sub>1</sub>–d<sub>7</sub>

Dye	DMSO	DMF	Acetonitrile	Methanol	Chloroform
d <sub>1</sub>	488	501	438	427	425
d <sub>2</sub>	456	475	432	363	347
d <sub>3</sub>	407	411	387	367	340
d <sub>4</sub>	433	479	417	397	355
d <sub>5</sub>	418	468	406	377	349
d <sub>6</sub>	428	409	409	342	340
d <sub>7</sub>	498	521	451	413	378

**Table 4** Effect of acid and base on the dyes d<sub>1</sub>–d<sub>7</sub>

Dye	$\lambda_{\max}$ (nm) Methanol	$\lambda_{\max}$ (nm) Methanol + 0.5 M NaOH	$\lambda_{\max}$ (nm) Methanol + 0.5 M acetic acid
d <sub>1</sub>	440	480, 520 s	401
d <sub>2</sub>	363	398, 423 s	637
d <sub>3</sub>	367	397, 456 s	346
d <sub>4</sub>	397	420, 488 s	364
d <sub>5</sub>	377	391, 423 s	348
d <sub>6</sub>	342	375, 433 s	331
d <sub>7</sub>	413	450, 488 s	388

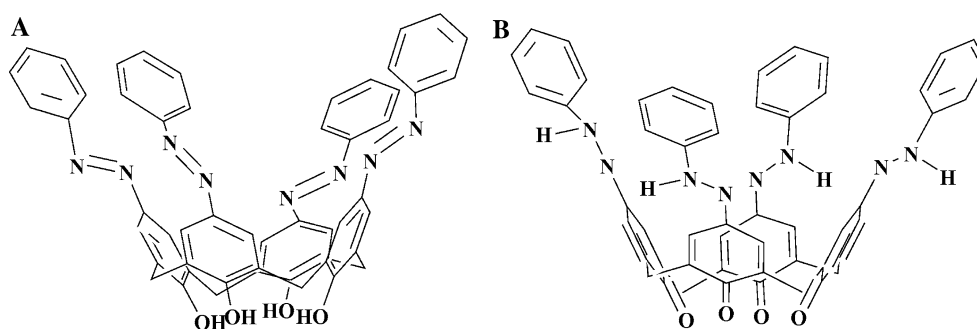
and methanol, the compounds displayed a red shift of  $\lambda_{\max}$ .

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.

#### Effect of acid and base

The effect of acid and base on the absorption of the dye solutions was investigated and the results are shown in Table 4. With the addition of base (0.1 M sodium hydroxide), the  $\lambda_{\max}$  of the dyes showed a hypsochromic shift along with a shoulder at longer wavelength. The  $\lambda_{\max}$  of the compounds in methanol also showed slightly hypsochromic effects with addition of acid (50% acetic acid). 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 (d<sub>1</sub>–d<sub>7</sub>) may exist in two possible tautomeric forms, namely an azo-enol form A and keto-hydrazo B as shown in Fig. 1.

The effect of concentration of the compound on absorption maxima was examined. The  $\lambda_{\max}$  of all compounds did not change with compound concentration.



**Fig. 1** The tautomeric form of synthesized dye

**Table 5** Fastness properties of the dyes d<sub>1</sub>–d<sub>6</sub>

Dyes	Uncoated paper		Coated paper	
	Light fastness	Wet fastness	Light fastness	Wet fastness
d <sub>1</sub>	4	4–5	5	5–6
d <sub>2</sub>	4–5	4	6	5
d <sub>3</sub>	4–5	5–6	5–6	6
d <sub>4</sub>	5	4–5	4–5	5–6
d <sub>5</sub>	4–5	5	6	5
d <sub>6</sub>	5	4–5	4–5	6

1 very poor, 2 poor, 3 moderate, 4 fairly good, 5 good, 6 very good, 7 excellent and 8 outstanding

**Table 6** Fastness properties of the dye d<sub>7</sub>

Dye	Washing		Light fastness		Wet fastness		Acid perspiration		Alkaline perspiration	
	Cotton	Wool	Cotton	Wool	Cotton	Wool	Cotton	Wool	Cotton	Wool
d <sub>7</sub>	3–4	4	5	4–5	5	4–5	3–4	4	5	4

1 very poor, 2 poor, 3 moderate, 4 fairly good, 5 good, 6 very good, 7 excellent and 8 outstanding

### Fastness properties

The light fastness of the dyes on d<sub>1</sub>–d<sub>6</sub> substrates except uncoated paper was in the range of 4–5 while the wet fastnesses on d<sub>1</sub>–d<sub>6</sub> substrates were in the range of 5–6 respectively which is considered as good and very good. The light fastness on uncoated paper and coated paper is summarized in Table 5. Only water soluble dye d<sub>7</sub> was used for dyeing cotton and wool. The fastness testing involving dyed cotton on wet fastness, wash fastness, light fastness and perspiration fastness is summarized in Table 6.

### Conclusions

The present paper reports on the synthesis, characterization, absorption spectra and the industrial application of a series

of azocalix[4]arene compounds. The light fastness and wet fastness of all the synthesized dyes were found to be good and very good. The dyes were all stable up to 245 °C and hence can be effectively used in almost all kinds of inks.

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