

Synthesis and Investigation Absorption Features of Some Novel Hetarylazo Dyes Derived from Calix[4]resorcinarene

İzzet Şener^{1*}, Koray Şarkaya²

¹Pamukkale University, Faculty of Science-Arts, Department of Chemistry, 20017, Denizli, Turkey

²Düzce University, Faculty of Science-Arts, Department of Chemistry, 81620, Düzce, Turkey

*Corresponding author e-mail: isener@pau.edu.tr

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Abstract: In this study, several derivatives of amines were diazotized and coupled with 3-aminocrotonitrile to give 2-arylhydrazon-3-ketiminocrotonitrile. The synthesized components were then refluxed with hydrazine hydrate in ethanol to give a series of dyes 5-amino-4-arylazo-3-ethyl-1'*H*-Pyrazole. The synthesized dyes were diazotised and coupled with resorcinarene, which was obtained from condensation of between resorcinol and acetaldehyde, to give a new synthesis of azo dyes based on resorcinarene. The structures of synthesized dyes based on resorcinarene were characterized by spectral methods. The effect of varying solvents, acid and base upon the absorption spectra of resultant dyes has been investigated.

Key words: Resorcinarene, Azo Dyes, Absorption Spectra, Solvent Effect, Acid-Base Effect

Rezorsinaren Bazlı Azo Boyarmaddelerin Sentezi ve Absorpsiyon Özelliklerinin İncelenmesi

Özet: Bu çalışmada, çeşitli amin türevleri diazolanmış ve 3-aminokrotonitril ile kenetlenerek 2-arilhidrazon-3-ketiminokrotonitril bileşikleri elde edilmiştir. Elde edilen bileşikler, hidrazinhidrat ile etanol içerisinde reflaks edilerek bir seri 5-amino-4-arilazo-3-metil-1'*H*-pirazol boyaları elde edilmiştir. Elde edilen boyalar diazonlarak rezorsinol ve asetaldehit arasındaki kondenzasyondan elde edilen rezorsinaren bileşiği ile kenetlenmiş ve rezorsinaren bazlı azo boyarmaddeler sentezlenmiştir. Sentezlenen rezorsinaren bazlı azoboyarmaddelerin yapıları spektrofotometrik yöntemler kullanılarak incelendi. Sentezlenen boyarmaddelerin görünür bölge absorpsiyon spektrumları üzerine değişik çözücü, asit ve baz etkileri incelendi.

Anahtar kelimeler: Rezorsinaren, Azo Boyarmadde, Absorpsiyon Spektrumu, Çözücü Etkisi, Asit-Baz Etkisi

1. Introduction

Calix[4]resorcinarenes are well known macro cyclic molecular receptors synthesized by base-induced condensation of resorcines with formaldehyde. They are noted for their size-related selectivity in binding cation, anions and organic neutral molecules [1,2]. They have found application as macro cyclic receptor [3], as dendrimers in biological systems [4-6], nano-capsule [7], nanoparticles [8,9], optical chemo sensors [10], supramolecular tectons [11-13], host molecules [14,15], as components in liquid crystals [16,17], photo resists [18-20], selective membranes [21,22], surface reforming agents [23], HPLC stationary phase [24], as ion channel mimics [25], and metal ion extraction agents [26-28].

Azo compounds are the most widely used class of dyes due to their versatile application in various fields such as the dyeing of textile fibre and the coloring of differing materials, and for plastics, biomedical studies, and advanced applications in organic synthesis. Moreover, azo groups bring to calixarenes a chromogenic activity [29-30]. As a continuation of the earlier our work, we have synthesized thirteen new hetaryl-tetrakis azocalix[4]resorcinarene.

2. Experimental

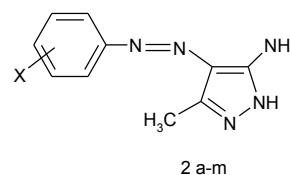
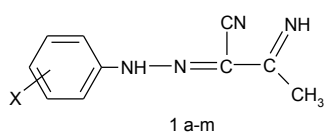
2.1. Materials

The chemicals used for the synthesis of the compounds were obtained from Aldrich (USA) and Merck Chemical Company (Germany) without further purification. Solvents were of spectroscopic grade. Melting points of the synthesis dyes were determined using stuart smp 30 melting point apparatus (UK). Nuclear magnetic resonance (¹H-NMR) spectra were recorded on a Bruker (Germany) Spectrospin Avance DPX 400 Ultra-Shield 400 MHz spectrometer at room temperature in deuterated dimethyl sulfoxide (DMSO-d₆) using tetramethylsilane (TMS) as the internal standard. Chemical shifts were (δ) given in ppm. FT-IR spectra were recorded on a Mattson (USA) 1000 FT-IR spectrometer as KBr pellets. UV-visible absorption spectra were recorded on an ATI (UK) Unicam UV-100 spectrophotometer over the range of λ between 300-700 nm. The wavelength of maximum absorption (λ_{max}) were investigated in a various solvents such as, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), acetonitrile, methanol, acetic acid and chloroform at various concentrations (1 x 10⁻⁶ – 1 x 10⁻⁸ M). Change of (λ_{max}) was also investigated when 0.1 mL of base (potassium hydroxide, 0.1 M) or 0.1 mL of acid (hydrochloric acid, 0.1 M) was added to 1 mL of the dye solution in methanol. Characterization data are shown in **Table 1**.

2.2. Synthesis

2.2.1. Synthesis of 2-arylhydrazone-3-ketiminobutyronitriles and 5-amino-4-arylazo-3-methyl-1H-pyrazoles

2-Arylhydrazone-3-ketiminobutyronitriles **1(a-m)** and 5-amino-4-arylazo-3-methyl-1H-pyrazoles **2(a-m)** were prepared according to the procedures given in literatures [31-39]. The structure of 2-arylhydrazone-3-ketiminobutyronitriles and 5-amino-4-arylazo-3-methyl-1H-pyrazoles is outlined in **Scheme 1**.

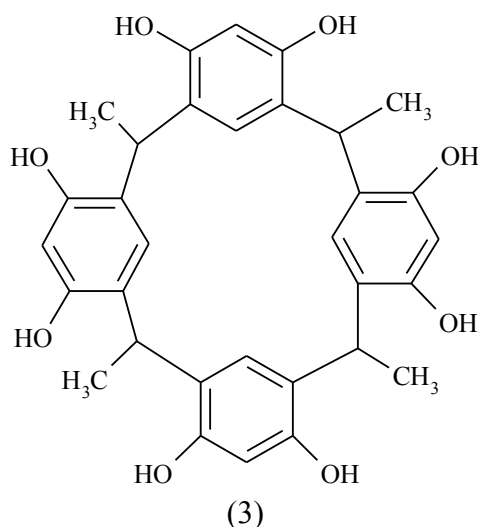


- | | | | |
|--------------------------|--------------------------|--------------------------|-------------------------|
| a; X: H | e; X: o-CH ₃ | i; X: m-CH ₃ | m; X: p-CH ₃ |
| b; X: o-NO ₂ | f; X: m-NO ₂ | j; X: p-NO ₂ | |
| c; X: o-OCH ₃ | g; X: m-OCH ₃ | k; X: p-OCH ₃ | |
| d; X: o-Cl | h; X: m-Cl | l; X: p-Cl | |

Scheme 1. The structure of 2-arylhydrazone-3-ketiminobutyronitriles and 5-amino-4-arylaazo-3-methyl-1H-pyrazole derivatives

2.2.1. Synthesis of 2,8,14,20-tetramethyl-4,6,10,12,16,18,22,24-oktahydroxycalix[4]rezorsinarene

2,8,14,20-Tetramethyl-4,6,10,12,16,18,22,24-oktahydroxycalix[4]rezorsinarene (3), were synthesized as described by a previously reported method [40-43]. The structure of substances is showed in **Scheme 2**.



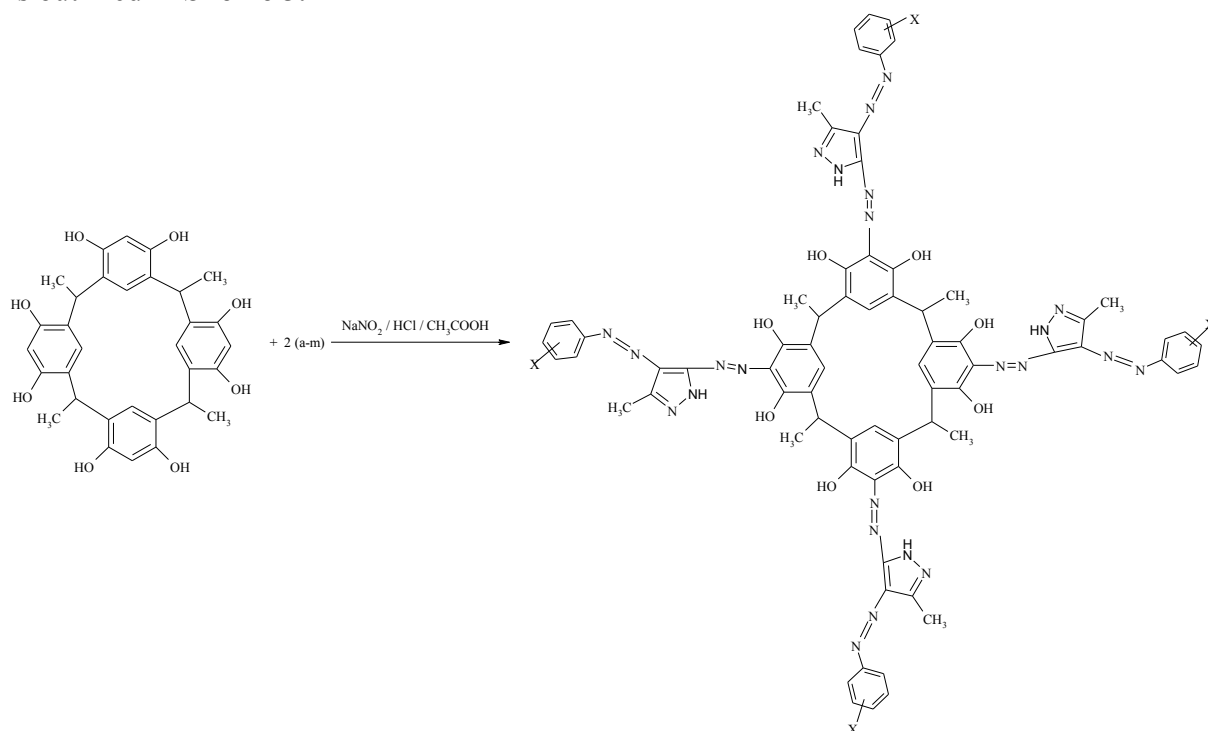
Scheme 2. The structure of resorcinarene

2.2.2. General synthesis of hetaryltetrakisazocalix[4]resorcinarene derivatives 4(a-m)

A general preparative procedure is described for the preparation of dye 5a. All other dyes (**4b-4m**) were prepared in similar manner.

5-Amino-3-methyl-4-phenylazo-1H-pyrazole (**2a**) (0.148 g ,0.736 mmol) was dissolved in a mixture of glacial acetic acid and concentrated hydrochloric acid (10 mL, ratio 1:1) and the solution was then cooled to 0–5 °C. Sodium nitrite (0.051 g, 0.736 mmol) in water (10 mL) was then added to this solution dropwise with vigorous stirring, during

about 1 h, while cooling at 0–5 °C. The clear diazonium salt solution was poured in portions over 30 min. into well-cooled (0–5 °C) and stirred solution of 2,8,14,20-Tetramethyl-4,6,10,12,16,18,22,24-oktahydroxycalix[4]rezorsinarene 0.1 g (0.1841 mmol) in DMF . By simultaneous addition of sodium acetate, the pH of the reaction mixture was maintained at 7.0-8.0. Stirring was continued for 4 h at 0–5 °C and the precipitated products separated upon dilution with cold water (50 mL) were filtered off, washed with water several times, dried. The obtained product was recrystallized from dimethylformamide-water mixture (2:3 by volume) to give 5,11,17,23-tetra-[3'-methyl-(4'-phenylazo-1'*H*-pyrazole-5'-ylazo) - 4,6,10,12,16,18,22,24-oktahydroxycalix[4]resorcinarene (**5a**). as yellow crystals, yield 0.174 g (68%), mp> 158 °C dec. General route for the synthesis of hetaryl-tetrakis azocalix[4]resorcinarene derivatives **4(a-m)** is outlined in **Scheme 3**.



Scheme 3. General route of hetaryl-tetrakis azocalix[4]resorcinarene derivatives

Table 1. Spectral data for dyes **4(a-m)**

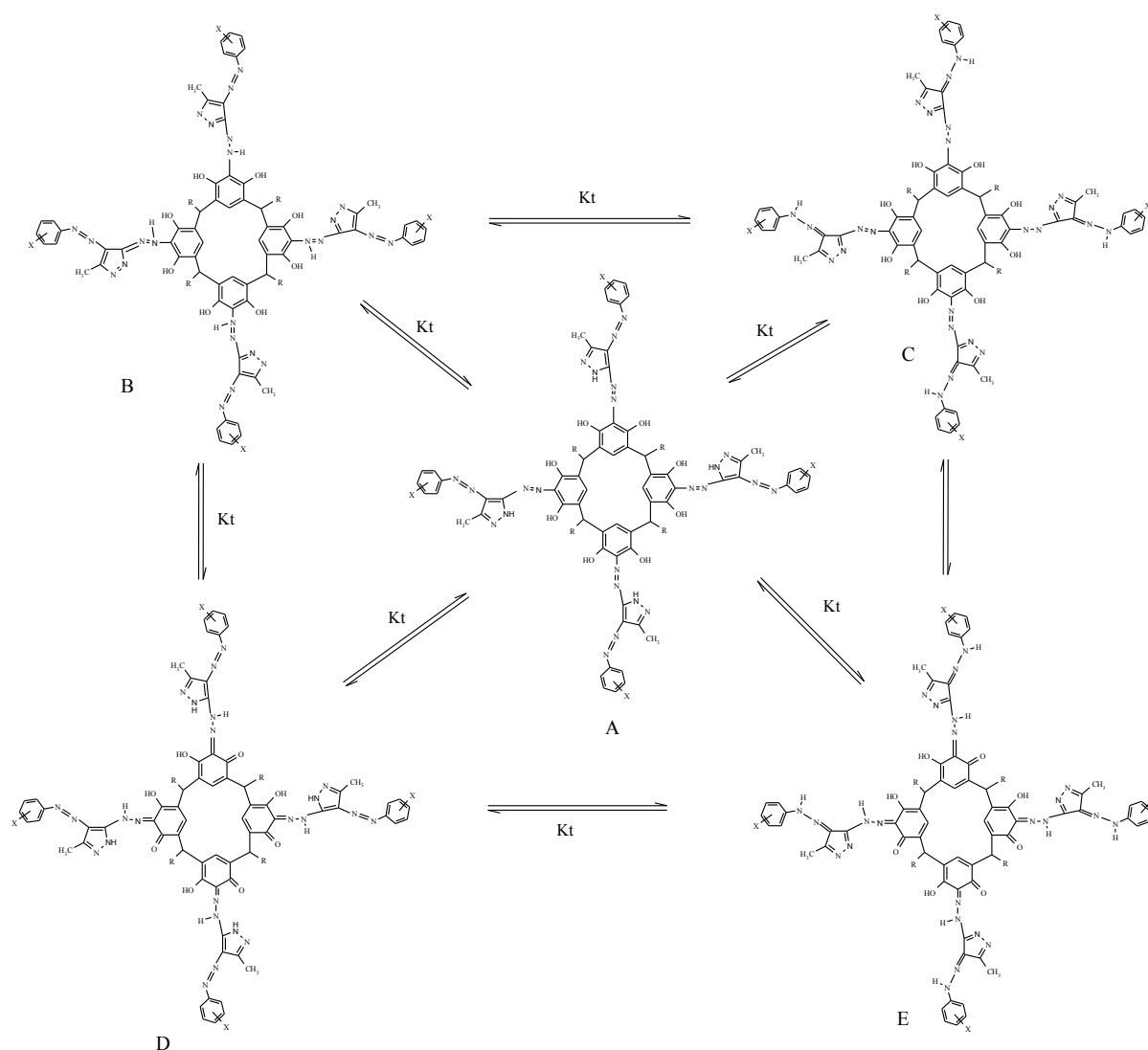
Dye no.	IR (cm ⁻¹) in KBr							¹ H-NMR (δ, ppm)			
	V _{O-H}	V _{C-H(aro.)}	V _{C-H(alip.)}	V _{C=C}	V _{N=N}	V _{NO₂}	V _{C-O}	Ar-H, N-H	Alip-H	O-H, Tautomeric N-H	Solvent
4a	3422	3030	2930-2960	3192	1587	-	1071	7.40-7.79 (m, 28H)	4.35 (m, 4H, -CH-), 2.64 (s, 3H, pyrazole-CH ₃), 1.25 (d, -CH ₃)	7.90 (s, 8H)	DMSO-d ₆
4b	3300	3020	2920-2950	3198	1616	1508 1336	1104	7.35-7.85 (m, 24H)	4.38 (m, 4H, -CH-), 2.70 (s, 3H, pyrazole-CH ₃), 1.27 (d, -CH ₃) 4.30 (m, 4H, -CH-), 2.60 (s, 3H, pyrazole-CH ₃), 2.85 (s, 3H, -OCH ₃), 1.27 (d, -CH ₃)	8.10 (s, 8H)	DMSO-d ₆
4c	3411	3016	2934-2990	3197	1601	-	1091	7.45-7.90 (m, 24H)	4.32 (m, 4H, -CH-), 2.70 (s, 3H, pyrazol-CH ₃), 1.25 (d, -CH ₃)	8.40 (s, 8H)	DMSO-d ₆
4d	3402	3020	2930-2996	3026	1629	-	1088	7.05-7.60 (m, 24H)	4.40 (m, 4H, -CH-), 2.65 (s, 3H, pyrazole-CH ₃), 2.60 (s, 3H, -OCH ₃), 1.20 (d, -CH ₃)	8.45 (s, 8H)	DMSO-d ₆
4e	3401	3010	2970-2996	3200	1602	-	1102	6.90-7.40 (m, 24H)	4.28 (m, 4H, -CH-), 2.74 (s, 3H, pyrazole-CH ₃), 1.26 (d, -CH ₃)	8.55 (s, 4H) 9.44 (s, 4H, N-H)	DMSO-d ₆
4f	3350	3012	2930-2960	3160	1617	1526 1350	1102	7.30-7.85 (m, 24H)	4.31 (m, 4H, -CH-), 2.65 (s, 3H, pyrazole-CH ₃), 2.87 (s, 3H, -OCH ₃), 1.27 (d, -CH ₃)	8.15 (s, 8H)	DMSO-d ₆
4g	3392	3010	2950-2970	3206	1529	-	1097	7.45-7.85 (m, 24H)	4.30 (m, 4H, -CH-), 2.70 (s, 3H, pyrazole-CH ₃), 1.25 (d, -CH ₃)	8.30 (s, 8H)	DMSO-d ₆
4h	3393	3015	2950-2990	3215	1614	-	1099	7.05-7.60 (m, 24 H)	4.30 (m, 4H, -CH-), 2.65 (s, 3H, pyrazole-CH ₃), 2.68 (s, 3H, -OCH ₃), 1.25 (d, -CH ₃)	8.45 (s, 8H)	DMSO-d ₆
4i	3396	3020	2960-2990	3209	1617	-	1102	6.90-7.45 (m, 24H)	4.31 (m, 4H, -CH-), 2.75 (s, 3H, pyrazole-CH ₃), 1.25 (d, -CH ₃)	8.50 (s, 8H)	DMSO-d ₆
4j	3421	3015	2960-2980	3206	1578	1528 1369	1097	7.30-8.05 (m, 24 H)	4.28 (m, 4H, -CH-), 2.65 (s, 3H, pyrazole-CH ₃), 2.80 (s, 3H, -OCH ₃), 1.25 (d, -CH ₃)	8.01 (s, 8H)	DMSO-d ₆
4k	3386	3010	2930-2970	3208	1589	-	1020	6.95-7.35 (m, 24H)	4.28 (m, 4H, -CH-), 2.75 (s, 3H, pyrazole-CH ₃), 1.25 (d, -CH ₃)	8.45 (s, 8H)	DMSO-d ₆
4l	3393	3015	2930-2976	3205	1601	-	1102	7.00-7.55 (m, 24H)	4.32 (m, 4H, -CH-), 2.75 (s, 3H, pyrazole-CH ₃), 2.65 (s, 3H, -OCH ₃), 1.25 (d, -CH ₃)	8.40 (s, 8H)	DMSO-d ₆
4m	3421	3018	2928-2960	3200	1541	-	1095	7.00-7.50 (m, 24H)	4.32 (m, 4H, -CH-), 2.75 (s, 3H, pyrazole-CH ₃), 2.65 (s, 3H, -OCH ₃), 1.25 (d, -CH ₃)	7.95 (s, 8H)	DMSO-d ₆

s : singlet, m : multiple, b : broad

3. Results and Discussion

In our earlier studies, carbocyclic and heterocyclic amine substituted azocalix[4]arenes [44-50] were investigated. As a continuation of our early work, in this paper, the synthesis of some tetrakisazocalix[4]resorcinarene derivatives **4(a-m)** have been reported. The compounds of thirteen new hetaryltetrakisazocalix[4]resorcinarenes **4(a-m)** were prepared by coupling 2,8,14,20-Tetramethyl-4,6,10,12,16,18,22,24-oktahydroxycalix[4]rezorsinarene with diazotized heterocyclic amines **2(a-m)**. Firstly, 2,8,14,20-Tetramethyl-4,6,10,12,16,18,22,24-oktahydroxycalix[4]rezorsinarene was prepared by reaction of resorcline with acetaldehyde according to the method given in reported literature [40-43]. Secondly, we synthesized 2-arylhydrazone-3-ketiminobutyronitriles **1(a-m)** and 5-amino-4-arylaazo-3-methyl-1-H-pyrazoles **2(a-m)** according to the procedures given in literatures [14-22]. Afterwards, The heterocyclic diazonium salts were derived from heterocyclic amines **2(a-m)**. Later, 2.0 equivalent heterocyclic diazonium salts **2(a-m)** reacted with 0.5 equivalent of 2,8,14,20-tetramethyl-4,6,10,12,16,18,22,24-oktahydroxycalix[4]rezorsinarene in DMF mixture to obtain the corresponding hetaryltetrakisazocalix[4]resorcinarene derivatives **4(a-m)**. These general reactions are shown in **scheme 3**. By the purification of the reaction mixtures, the thirteen hetaryltetrakisazocalix[4]resorcinarene derivatives have been obtained in 60-81 % yield.

The obtained products from the above mentioned reactions were characterized using FT-IR and ¹H-NMR spectral data. The hetaryltetrakisazocalix[4]resorcinarene derivatives **4(a-m)** may exist in five possible tautomeric forms which are a diazo-phenol form, a azo -hydrazone-phenol form, a hydrazone-azo-phenol forms, a azo-hydrazone-quinone form and a dishydrazone-quinone form named **A**, **B**, **C**, **D** and **E**, respectively, as shown in **Scheme 4**. The infrared spectra of all the compounds **4(a-m)** showed a band in the range of 3300-3422 cm⁻¹ corresponding to ν_{OH} and a band located at 3010-3030 cm⁻¹ assigned to aromatic C-H. The others ν_{max} values at 3160- 3215 cm⁻¹ N-H, 2930-2980 cm⁻¹ aliphatic C-H, 1529-1629 cm⁻¹ (N=N), 1072-1104 cm⁻¹ (C-O) were also recorded. Because of the infrared spectra of all compounds showed -OH bands at 3300-3422 cm⁻¹ and (C-O) bands 1071-1104 cm⁻¹, it can be suggested that these compounds exist as the phenol forms in **A**, **B** and **C** in the solid state. On the other hand, **4a** and **4e** compounds showed C=O band at 1774 cm⁻¹ and 1784 cm⁻¹, respectively. According to this result, we can say that the compound **4a** and **4e** can be exist as the quinone forms in **D** and **E** in the solid state.



Scheme 4. The tautomeric form of hetaryl-tetrakisazocalix[4]resorcinarene derivatives.

The structures of **4(a-m)** were examined by using high-resolution NMR. The $^1\text{H-NMR}$ spectra were measured in DMSO-d_6 at 25°C . The $^1\text{H-NMR}$ spectra of all compounds showed doublet peak for methyl ($\text{CH}_3\text{-CH-}$) protons at between 1.20-1.27 ppm, multiple peak for (-CH-CH_3) protons at between 4.28-4.40 ppm and singlet peak for methyl protons (pyrazole- CH_3) at between 2.65-2.75 ppm. The **4e**, **4i**, **4m** compounds showed singlet peak for methyl protons (Ar-CH_3) at between 2.60-2.68 ppm. The **4c**, **4g**, **4k** compounds showed two singlet peak for methyl protons (Ar-OCH_3) at between 2.80-2.87 ppm. All compounds **4(a-m)** showed a multiplet peak at between 6.90-8.05 ppm for aromatic protons (Ar-H), a singlet peak at between 7.90-8.55 ppm for hydroxyl proton (-OH). The $^1\text{H-NMR}$ spectra of dye **4e** showed a broad peak at between 9.44 ppm for tautomeric hydrazo (-NH) proton. The $^1\text{H-NMR}$ spectra all of the dyes showed only NH proton, but did not showed hydrazo NH proton except for **4e**. According to $^1\text{H-NMR}$ results, dyes named as **4e** have a mixture of azo-hydrazone-

phenol (**B**), hydrazone-azo-phenol (**C**), a azo-hydrazone-quinone (**D**) and dishydrazone-quinone (**E**) tautomeric forms, but not diazo-phenol (**A**) tautomeric form in DMSO- d_6 as showed in **Scheme 4**.

UV-Visible analysis

In general, tautomeric equilibrium strongly depends on the nature of the media. Therefore, the behaviour of tetrakisazo dyes was studied in various solvents. Because of solubility problems, the absorption spectra of disazo dyes **4(a-m)** were measured in various solvents at a concentration of approximately (10^{-6} - 10^{-8} M). Solvents used for the U.V. measurements have different dielectric constants (ϵ), i.e. DMSO (ϵ ,46.45), DMF (ϵ , 36.71), acetonitrile (ϵ , 35.94), methanol (ϵ , 32.66), acetic acid (ϵ , 6.17) and chloroform (ϵ , 4.89) [50]. The results obtained from the absorption measurements are given in **Table 2**. The visible absorption spectra of the dyes did not have correlation with the polarity of solvents. Only plausible explanation for this irregular behavior may be due to the supramolecular structure of these dyes with intramolecular hydrogen bonding, having great potential of interacting with the solvents molecules through non-covalent or non-conventional interactions. Alternatively, it can be thought that these types of supramolecular structures usually bind or encapsulate solvent molecules into their cavity and thereby prevent to exhibit regular solvatochromic effect . It is known that, the ground state for nearly all molecules is less polar than excited state so that a polar solvent will tend to stabilize in the excited state more than ground state [51]. It was found that, as the polarity of the solvents was increased with the increasing dielectric constant of the solvents, the absorption maxima of the dyes generally indicates small bathochromic shifts. The dyes generally showed bathochromic shifts in most polar solvents, such as DMSO and DMF. The spectral shifts of dye **4b** in various solvents are depicted in **Fig.1** and **Fig.2**, respectively. There is no significant change in the absorption spectra of the dyes in acetonitrile and methanol except for dye **4f**.

Table 2. Influence of solvent on λ_{\max} (nm) of dyes **4(a-m)**

Dye no.	DMSO	DMF	Acetonitrile	Methanol	Acetic acid	Chloroform
4a	338,420s	342,434s	328,390s	327,420s	335,430	328,418s
4b	365,470	364,455	355o,426	352o,425	359,490s	342o,410
4c	353,480s	351,468s	343,422s	342,425s	346,452s	345,430s
4d	343,472s	340,470s	334,422s	335,425s	334,418s	338,398s
4e	344,470s	343,470s	336,415s	336,425s	328,418s	341,470s
4f	338,460s	337,465s	331,422s	337,420s	333,420s	333,421s
4g	341,475s	341,475s	329,421	328,419s	331,420s	331,421s
4h	341,460	340,475	331,419s	331,422	339,418s	333,420s
4i	339,475s	338,470s	331,419s	330,418s	339,420	332,422s
4j	342,475s	341,470s	336,455s	334,430s	334,455s	339,421s
4k	357,460s	359,460	350,420s	350,425s	433,582s	373
4l	339,440s	340,480s	330,418s	332,435s	337o,425	331,390s
4m	341,457	341,456	337,430s	336,425s	334,423s	339,420s

s : shoulder

It was observed that λ_{\max} values of dyes in DMSO and DMF were shifted bathochromically with respect to the λ_{\max} in methanol except for **4i** and **4l**. λ_{\max} values of dyes in DMF were shifted bathochromically with respect to the λ_{\max} in methanol except for **4f**. For example; the absorption maxima of **4b** was observed at 359 nm in acetic acid, 365 and 470 nm in DMSO, 364 and 455 nm in DMF and 425 nm in methanol, respectively (**Fig.1**).

The absorption spectra of prepared dyes showed a maximum absorption peak with a shoulder in all solvents except for **4k** in methanol. The dye **4a** in chloroform showed only a maximum absorption peak. The dyes **4a** in acetic acid, **4b** in DMSO and DMF, **4g** in acetonitrile, **4h** in DMSO,DMF and methanol, **4i** in acetic acid, **4k** in DMF, 4m in DMSO and DMF showed two maximum absorption peak. It suggests that these dyes present more than one tautomeric form. Typical examples of these results are given in **Fig.1**.

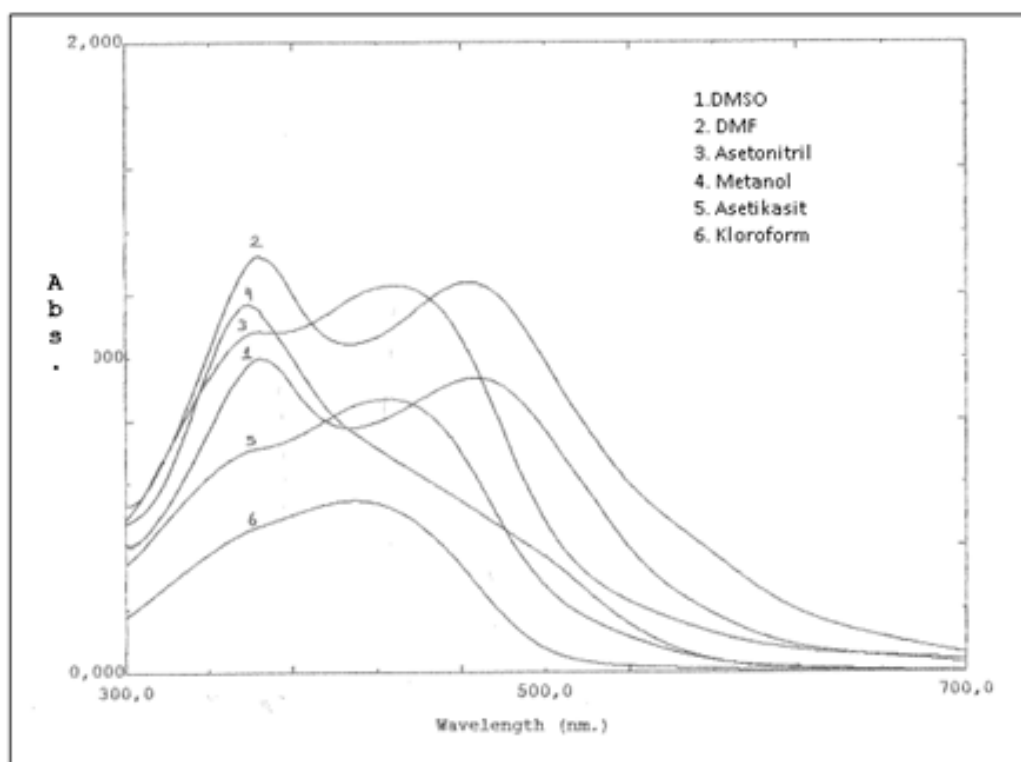


Figure 1. Absorption spectra of dye 4b in various solvents.

The effects of the acid and base on the absorption spectrum of the dyes solutions were investigated and the results were depicted in **Table 3**.

Table 3. Absorption maxima of dyes **4(a-m)** in acidic and basic solutions

Dye no.	Methanol	Methanol + HCl	Methanol + KOH
4a	327,420s	325,415s	355,425s
4b	425, 352s	360	457
4c	342,425s	343,450s	361,421s
4d	335,425s	331,450s	359,550s
4e	336,425s	333,430s	349,430s,
4f	337,420s	335,419s	374,425s
4g	328,419s	326,420s	363,425s
4h	331,422s	330,418s,	361,430s
4i	330,418s	325,422s	356,455s
4j	334,430s	325,420s	361,580s
4k	350,425s	328,375s	359,575s
4l	332,435s	325,445s	350,450s
4m	336,425s	329,422s	354,545s

s : shoulder

The absorption spectra of the dyes in methanol were quite sensitive to the addition of base (potassium hydroxide, 0.1 M). Therefore, the λ_{\max} of dyes **4(a-m)** showed a bathochromic shifts with the addition of base to methanol. For example; λ_{\max} of **4b** was recorded at 425 nm a maximum absorption and 352 nm a shoulder in methanol, 457 nm in methanol + KOH (**Fig.2**).

When hydrochloric acid (0.1 M) was added to the dye solutions in methanol, hypsochromic shifts were detected, except for **4c**. The λ_{\max} of **4b** was observed at 360 nm in 409 nm in methanol + HCl. These results indicate that the tautomeric form in methanol changed with another tautomeric form in acidic and basic solution (**Fig 2**).

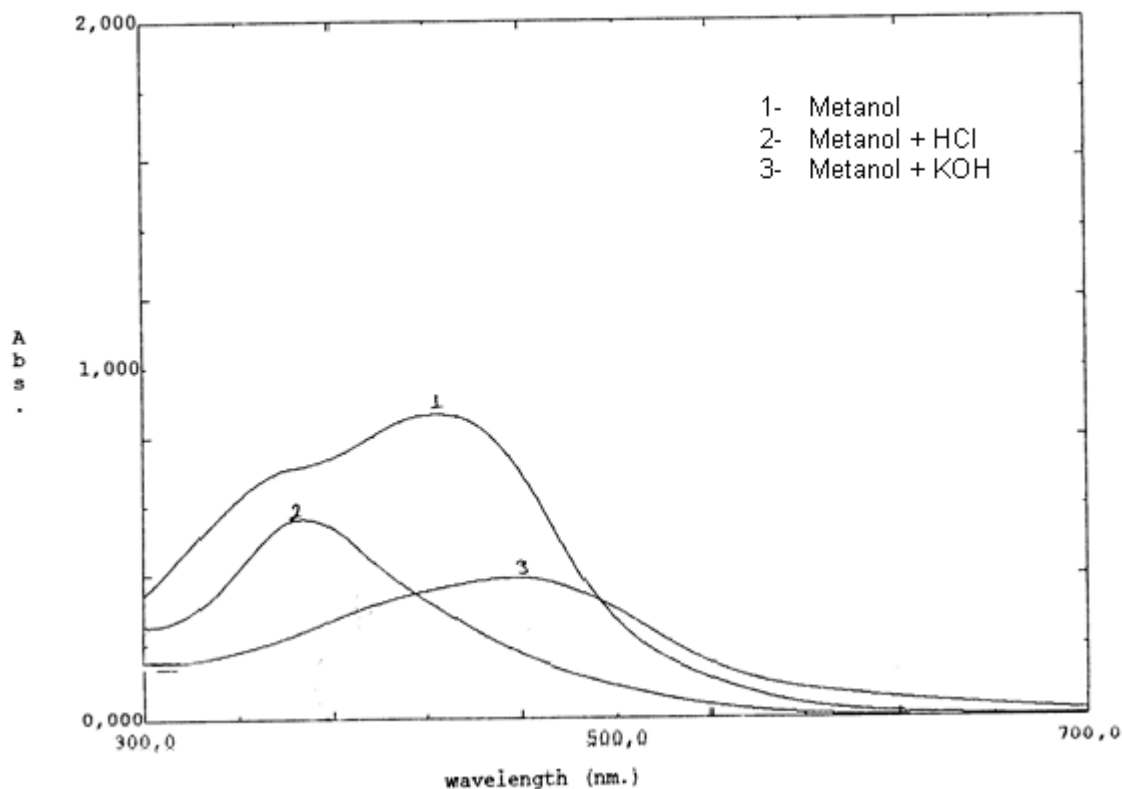


Figure 2. Absorption spectra of dye 4b in acidic and basic solutions.

4. Conclusion

In summary, the synthesis and characterization of thirteen novel hetaryltetrakisazocalix[4]resorcinarene based dyes **4(a-m)** were studied by means of FT-IR, ¹H-NMR and Mass spectroscopic techniques. The heterocyclic diazonium salts were derived from heterocyclic amines **2(a-m)**, and reacted with 0.5 equivalent of 2,8,14,20-Tetramethyl-4,6,10,12,16,18,22,24-oktahydroxycalix[4]rezorsinarene in DMF to afford 5,11,17,23-tetra-[3'-methyl-(4'-phenylazo-1'*H*-pyrazole-5'-ylazo)-4,6,10,12,16,18,22,24-oktahydroxycalix[4] resorcinarene **4(a-m)**. We have synthesized a new chromogenic azocalix[4]resorcinarene dyes. The FT-IR and ¹H-NMR spectra results of hetaryltetrakisazocalix[4]resorcinarene dyes **4(a-m)** revealed that these compounds exist in forming different tautomeric forms.

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Koray Şarkaya e-mail: koraysarkaya@duzce.edu.tr