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Synthesis and absorption spectra of some novel hetaryltetrakisazocalix[4]arene derivatives

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ABSTRACT

In this study, a convenient method for the synthesis of thirteen novel tetrakisazo dyes containing 25,27-bis-(4-nitrobenzyloxy)-26,28-dihydroxycalix[4]arene have been described. 5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene, 25,26,27,28-tetrahydroxycalix[4]arene and 25,27-bis-(4-nitrobenzyloxy)-26,28-dihydroxycalix[4]arene were synthesized. 2-arylhydrazone-3-ketiminobutyronitriles **1(a–m)** were synthesized and reacted with hydrazine hydrate to afford the corresponding 5-amino-4-arylazo-3-methyl-1-H-pyrazoles **2(a–m)**. Thirteen novel hetaryltetrakisazocalix[4]arene derivatives **6(a–m)** were achieved by diazotisation of 5-amino-4-arylazo-3-methyl-1-H-pyrazoles using nitrosylsulphuric acid, coupling with 25,27-bis-(4-nitrobenzyloxy)-26,28-dihydroxycalix[4]arene. The obtained hetaryltetrakisazocalix[4]arene dyes **6(a–m)** were characterized based on FT-IR, ^{1}H NMR and Mass spectroscopic techniques as well as Elemental Analysis. The solvatochromic behaviour of these dyes in various solvents was examined. Acid-base effect on the visible absorption maxima of the dyes were also reported.

1. Introduction

The developing field of supramolecular chemistry was launched by the discovery of an important class of macrocyclic compounds called calixarene. Calixarenes have received considerable attention in the past decade in host–guest or supramolecular chemistry [1].

Calixarenes are cyclic oligomers made of several phenolic units bounded with methylene bridges. It can exist in the conformations cone, partial cone, 1,2-alternate and 1,3-alternate [2,3].

Calixarenes and their derivatives can be used as synthetic receptors to selectively bind a wide variety of guest molecules/ions forming host–guest complexes or supramolecular species, and have been applied successfully to various areas of science and technology. It is also noted that the calixarene platform can be selectively functionalized both at the phenolic OH groups (lower rim) [4] and at the para positions of the phenol rings (upper rim), which provides unique possibilities to organize several binding sites appropriately for complexation of potential guests [5].

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 colouring of differing materials, and for plastics, biomedical studies, and advanced applications in organic synthesis. Moreover, azo groups bring to calixarenes a chromogenic activity [6,7].

Substances that change colour or change fluorescence in response to a change in their environment are an integral part of nature and have been put to human use since antiquity, a modern example of long standing being the application of indicator compounds to measure acidity and basicity. In recent years increasing attention has been paid to such chromogenic molecules, and a number of calixarene based systems have been studied [2].

Aminopyrazoles are very important class of heterocycles because of their biological and pharmacological activities. For example, pyrazolopyrimidines and related fused heterocycles are of interest as potential bioactive molecules. Some azopyrazole derivatives can also be used in dyes, biological and pharmacological studies and complexes [8–13]. These compounds can be obtained by the reaction of nitriles with hydrazine hydrate [14–22].

Despite of the fact that dyeing properties and synthesis of monoazo dyes based on heterocyclic diazo component [23–27], and chromogenic calixarenes [28–35], previously have been reported, any investigation involved in hetaryltetrakisazo derivatives based on 25,27-bis-(4-nitrobenzyloxy)-26,28-dihydroxycalix[4]arene have not been found. As an extension of our previous work in this area [36–41], in this study we report the synthesis of a series of new hetaryltetrakisazo dyes based on calix[4]arene **6(a–m)**.

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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 (^{1}H NMR) spectra were recorded on a Bruker (Germany) Spectrospin Avance DPX 400 Ultra-Shield 400 MHz spectrometer at room temperature in deuterated dimethylsulphoxide (DMSO-d_6) 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. LC–ESI-MS analyses were recorded on an Agilent (Germany) 1100 MSD. Elemental analyses were done on a Leco CHNS-932 analyser. UV–visible absorption spectra were recorded on an ATI (UK) Unicam UV-100 spectrophotometer over the range of λ between 300 and 700 nm. The wavelength of maximum absorption (λ_{max}) was investigated in a various solvents such as, dimethylsulphoxide (DMSO), dimethylformamide (DMF), acetonitrile, methanol, acetic acid and chloroform at various concentrations (1×10^{-6}–1×10^{-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.

2.2. Synthesis

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene **(3)** [42], 25,26,27,28-tetrahydroxycalix[4]arene **(4)** [43] and 25,27-bis-(4-nitrobenzyloxy)-26,28-dihydroxy calix[4]arene **(5)** were synthesized as described by a previously reported method [44].

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

2-Arylhydrazone-3-ketiminobutyronitriles **1(a–m)** and 5-amino-4-arylazo-3-methyl-1-H-pyrazoles **2(a–m)** were prepared according to the procedures given in literature [14–22]. The structure of 2-arylhydrazone-3-ketiminobutyronitriles and 5-amino-4-arylazo-3-methyl-1-H-pyrazoles is outlined in Fig. 1.

2.2.2. General synthesis of hetaryltetrakisazocalix[4]arene derivatives ***6(a–m)***

Nitrosylsulphuric acid was prepared by dissolving sodium nitrite 0.138 g (2.0 mmol) in concentrated sulphuric acid (4.0 mL) at 70 °C and was cooled down to −5 °C. 5-amino-3-methyl-4-arylazo-1-H-pyrazole **2(a–m)** (2.0 mmol) was dissolved in hot glacial acetic acid (4 mL) and rapidly cooled in ice bath to −5 °C. The nitrosylsulphuric acid at between 0 and 5 °C was poured in portions over 30 min into this solution. The reaction mixture was stirred for 2 h at this temperature. The resulting diazonium solution was added in portions over 30 min to a vigorously stirred solution of 25,27-bis-(4-nitrobenzyloxy)-26,28-dihydroxycalix[4]arene 0.694 g (1.0 mmol) in DMF/MeOH mixture (26 mL, 8:5, v/v). The progress of the reaction was followed by thin layer chromatography (TLC) using an ethylacetate:*n*-hexane mixture (1:1 by volume) as developing solvent and silica gel TLC plates as the stationary phase. By simultaneous addition of sodium acetate, the pH of the reaction mixture was maintained at 7.0–8.0 and the mixture was stirred for 2 h at between 0 and 5 °C. The resulting solid was filtered, washed with cold water and dried. The obtained product was crystallized from DMF–H_2O mixture (2:3 by volume). The structure of 5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene **(3)**, 25,26,27,28-tetrahydroxycalix[4]arene **(4)**, and 25,27-bis-(4-nitrobenzyloxy)-26,28-dihydroxycalix[4]arene **(5)** and the general route for the synthesis of hetaryltetrakisazocalix[4]arene derivatives **6(a–m)** is outlined in Fig. 2.

2.2.2.1. 25,27-bis-[(4-nitrobenzyloxy)-26,28-dihydroxy-5,17-bis-[3′-methyl-4′-phenylazo-1′-H-pyrazole-5′-ylazo]calix[4]arene (***6a***).

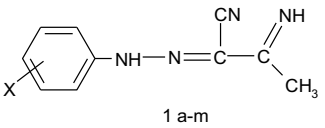
Light green solid, yield 0.69 g (62%), m.p: 145 °C. Anal. Cal. for $C_{62}H_{50}N_{14}O_8$; C: 66.55%; H: 4.47%; N: 14.53%; Found: C: 66.65%; H:4.52%; N: 14.58%. IR (KBr) υ (cm^{-1}): 3520 cm^{-1} (–OH), 3015–3027 cm^{-1} (Aromatic C–H), 2945–2960 cm^{-1} (Aliphatic C–H), 1575 cm^{-1} (N=N), 1090 cm^{-1} (C–O). ^{1}H NMR (DMSO-d_6, 25 °C) δ (ppm): 2.85, 3.10 (6H, s, pyrazole–CH_3), 3.51 and 4.27 (8H, d, $J = 13.2$ Hz, Ar–CH_2–Ar), 5.16 (4H, s, CH_2), 7.25 and 7.65 (2H, s, OH), 7.35–8.10 (28H, m, Ar–H), 9.50 (1H, broad, NH), 10.55 (1H, broad, NH). MS *m*/*z* (M^+): 1118.

2.2.2.2. 25,27-bis[(4-nitrobenzyloxy-26,28-hydroxy-5,17-bis-[3′-methyl-4′(2″-nitro phenylazo-1′-H-pyrazole-5′-ylazo]calix[4]arene (***6b***).

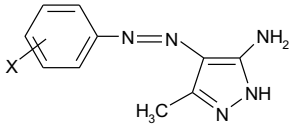
Light brown solid, yield 0.90 g (75%), m.p: 220 °C. Anal. Cal. for $C_{62}H_{48}N_{16}O_{12}$; C: 61.59%; H: 3.97%; N: 18.54%; Found: C: 61.63%; H: 4.01%; N: 18.58%. IR (KBr) υ (cm^{-1}): 3525 cm^{-1} (–OH), 3016–3029 cm^{-1} (Aromatic C–H), 2942–2958 cm^{-1} (Aliphatic C–H), 1576 cm^{-1} (N=N), 1521 cm^{-1} (NO_2), 1096 cm^{-1} (C–O). ^{1}H NMR (DMSO-d_6, 25 °C) δ (ppm): 2.91, 3.20 (6H, s, pyrazole–CH_3), 3.51 and 4.26 (8H, d, $J = 13.2$ Hz, Ar–CH_2–Ar), 5.20 (4H, s, CH_2), 7.20 and 7.65 (2H, s, OH), 7.25–8.20 (26H, m, Ar–H), 9.75 (1H, broad, NH), 11.20 (1H, broad, NH). MS *m*/*z* (M^+): 1208.

2.2.2.3. 25,27-bis-[(4-nitrobenzyloxy-26,28-dihydroxy-5,17-bis-[3′-methyl-4′(2″-methoxy phenylazo-1′-H-pyrazole-5′-ylazo]calix[4]arene (***6c***).

Yellow mustard solid, yield 0.82 g (70%), m.p: 130 °C. Anal. Cal. for $C_{64}H_{54}N_{14}O_{10}$; C: 65.19%; H: 4.58%; N: 16.63%; Found: C: 65.17%; H: 4.62%; N: 16.61%. IR (KBr) υ (cm^{-1}): 3526 cm^{-1} (–OH), 3012–3025 cm^{-1} (Aromatic C–H), 2945–2965 cm^{-1} (Aliphatic C–



1 a-m



2 a-m

a; X: H
b; X: o-NO_2
c; X: o-OCH_3
d; X: o-Cl
e; X: o-CH_3
f; X: m-NO_2
g; X: m-OCH_3
h; X: m-Cl
i; X: m-CH3
j; X: p-NO_2
k; X: p-OCH_3
l; X: p-Cl
m; X: p-CH_3

Fig. 1. The structure of 2-arylhydrazone-3-ketiminobutyronitriles and heterocyclic amine derivatives **2(a–m)**.

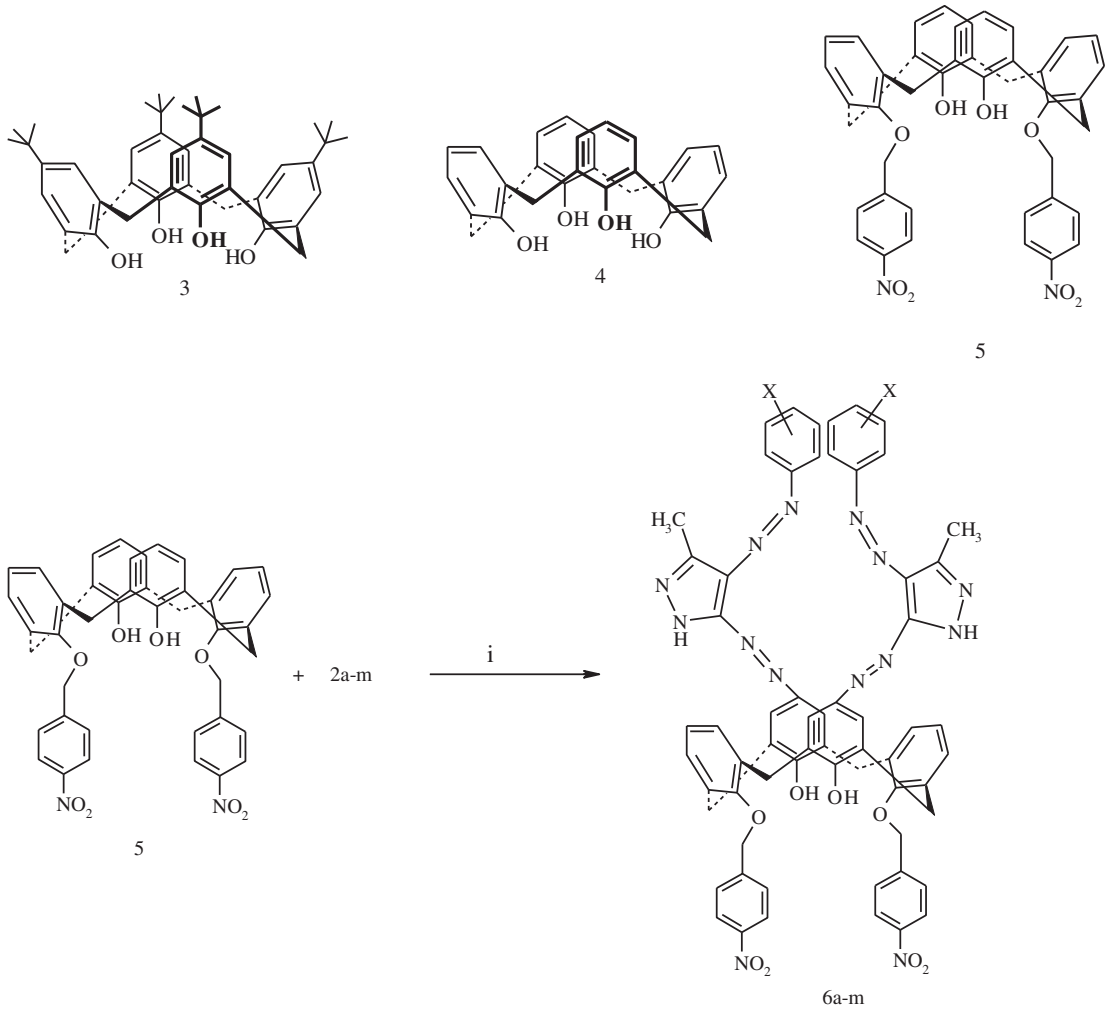


Fig. 2. The structure of **(3)**, **(4)**, **(5)** and the synthesis of tetrakishetarylazocalix[4]arene derivatives. (i) $NaNO_2/H_2SO_4$, CH_3COOH.

H), 1582 cm^{-1} (N=N), 1096 cm^{-1} (C–O). ^1H NMR (DMSO-d_6, 25 °C) δ (ppm): 2.89, 3.21 (6H, s, pyrazole–CH_3), 3.48 and 4.28 (8H, d, J = 13.2 Hz, Ar–CH_2–Ar), 4.10 (6H, s, Ar–OCH_3), 5.18 (4H, s, CH_2), 7.30 and 7.60 (2H, s, OH), 7.25–8.17 (26H, m, Ar–H), 9.72 (1H, broad, NH), 11.25(1H, broad, NH). MS m/z (M^+): 1178.

*2.2.2.4. 25,27-bis-[(4-nitrobenzyloxy-26,28-dihydroxy-5,17-bis-[3′-methyl-4′(2″-chloro phenylazo-1′-H-pyrazole-5′-ylazo]calix[4]arene (**6d**).* Yellow solid, yield 0.90 g (76%), m.p: 125 °C. Anal. Cal. for $C_{62}H_{48}N_{14}O_8Cl_2$; C: 62.68%; H: 4.04%; N: 16.51%; Found: C: 62.72%; H: 4.08%; N: 16.55%. IR (KBr) υ (cm^{-1}): 3528 cm^{-1} (–OH), 3015–3036 cm^{-1} (Aromatic C–H), 2950–2967 cm^{-1} (Aliphatic C–H), 1576 cm^{-1} (N=N), 1095 cm^{-1} (C–O). ^1H NMR (DMSO-d_6, 25 °C) δ (ppm): 2.92, 3.16 (6H, s, pyrazole–CH_3), 3.47 and 4.20 (8H, d, J = 13.2 Hz, Ar–CH_2–Ar), 5.22 (4H, s, CH_2), 7.25 and 7.70 (2H, s, OH), 7.25–8.15 (26H, m, Ar–H), 9.98 (1H, broad, NH), 11.35 (1H, broad, NH). MS m/z (M^+): 1187.

*2.2.2.5. 25,27-bis-[(4-nitrobenzyloxy-26,28-dihydroxy-5,17-bis-[3′-methyl-4′(2″-methyl phenylazo-1′-H-pyrazole-5′-ylazo]calix[4]arene (**6e**).* Orange solid, yield 0.72 g (63%), m.p: 134 °C. Anal. Cal. for $C_{64}H_{54}N_{14}O_8$; C: 67.01%; H: 4.71%; N: 17.10%; Found: C: 67.04%; H: 4.73%; N: 17.12%. IR (KBr) υ (cm^{-1}): 3528 cm^{-1} (–OH), 3012–3025 cm^{-1} (Aromatic C–H), 2943–2961 cm^{-1} (Aliphatic C–H), 1578 cm^{-1} (N=N), 1094 cm^{-1} (C–O). ^1H NMR (DMSO-d_6, 25 °C) δ (ppm): 2.88, 3.19 (6H, s, pyrazole–CH_3), 3.48 and 4.25 (8H, d, J = 13.2 Hz, Ar–CH_2–Ar), 4.07 (6H, s, Ar–CH_3), 5.25 (4H, s, CH_2), 7.22 and 7.68 (2H, s, OH), 7.26–8.20 (26H, m, Ar–H), 9.96 (1H, broad, NH), 11.95 (1H, broad, NH). MS m/z (M^+): 1146.

*2.2.2.6. 25,27-bis-[(4-nitrobenzyloxy-26,28-dihydroxy-5,17-[3′-methyl-4′(3″-nitro phenylazo-1′-H-pyrazole-5′-ylazo]calix[4]arene (**6f**).* Light yellow, yield 0.94 g (78%), m.p: 225 °C. Anal. Cal. for $C_{62}H_{48}N_{16}O_{12}$; C: 61.59%; H: 3.97%; N: 18.54%; Found: C: 61.62%; H: 3.99%; N: 18.57%. IR (KBr) υ (cm^{-1}): 3529 cm^{-1} (–OH), 3010–3032 cm^{-1} (Aromatic C–H), 2950–2970 cm^{-1} (Aliphatic C–H), 1578 cm^{-1} (N=N), 1524 cm^{-1} (NO_2), 1096 cm^{-1} (C–O). ^1H NMR (DMSO-d_6, 25 °C) δ (ppm): 2.90, 3.18 (6H, s, pyrazole-CH_3), 3.51 and 4.20 (8H, d, J = 13.2 Hz, Ar–CH_2–Ar), 5.18 (4H, s, CH_2), 7.23 and 7.62 (2H, s, OH), 7.26–8.22 (26H, m, Ar–H), 10.21 (1H, broad, NH), 12.35 (1H, broad, NH). MS m/z (M^+): 1208.

*2.2.2.7. 25,27-bis-[(4-nitrobenzyloxy-26,28-dihydroxy-5,17-[3′-methyl-4′(3″-methoxy phenylazo-1′-H-pyrazole-5′-ylazo]calix[4] arene (**6g**).* Light yellow, yield 0.74 g (63%), m.p: 120 °C. Anal. Cal. for $C_{64}H_{54}N_{14}O_{10}$; C: 65.19%; H: 4.58%; N: 16.63%; Found: C: 65.25%; H: 4.62%; N: 16.69%. IR (KBr) υ (cm^{-1}): 3525 cm^{-1} (–OH), 3014–3026 cm^{-1} (Aromatic C–H), 2946–2964 cm^{-1} (Aliphatic C–H), 1582 cm^{-1} (N=N), 1095 cm^{-1} (C–O). ^1H NMR (DMSO-d_6, 25 °C) δ (ppm): 2.98, 3.24 (6H, s, pyrazole–CH_3), 3.50 and 4.23 (8H, d,

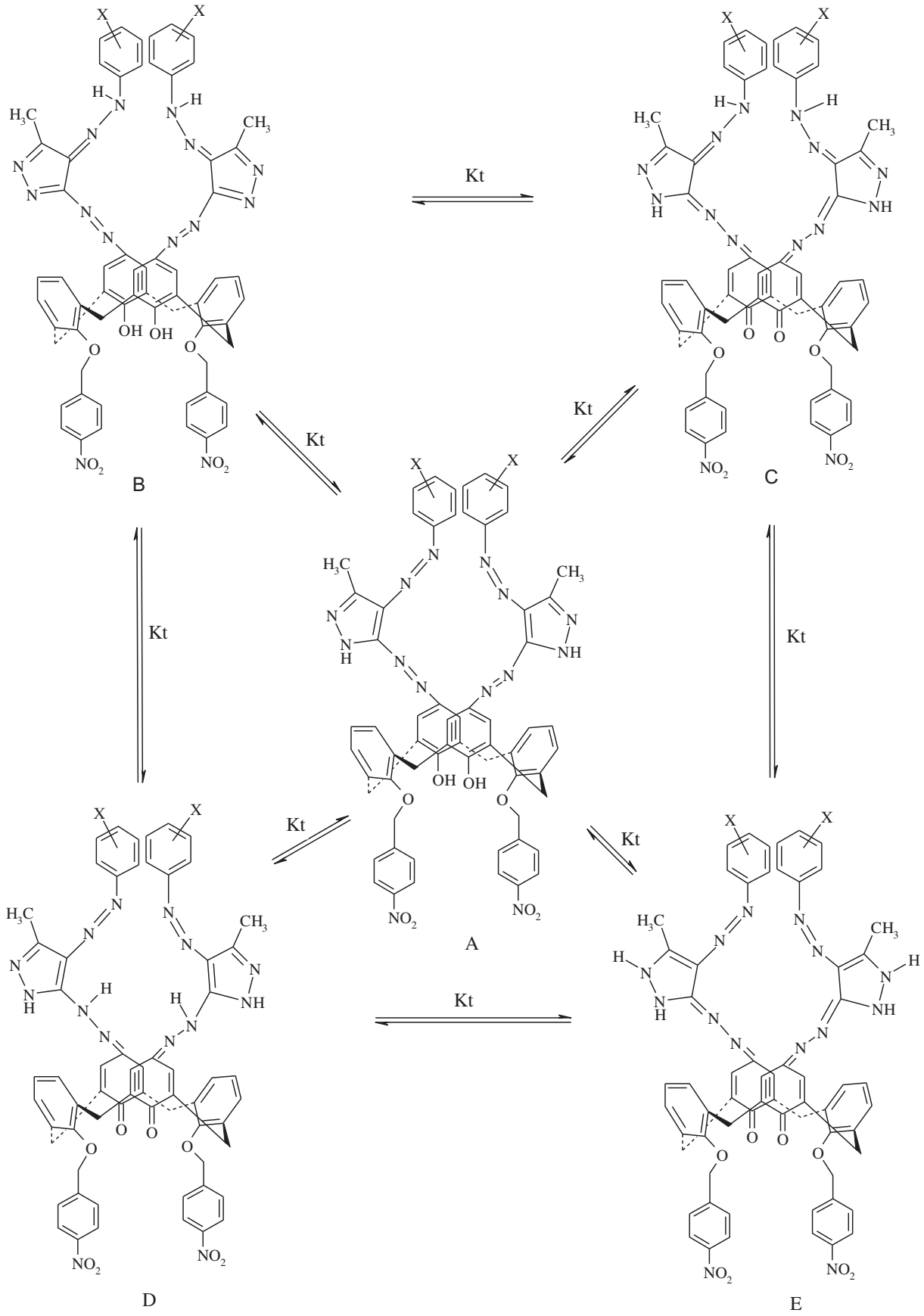


Fig. 3. The tautomeric form of tetrakishetarylazocalix[4]arene derivatives.

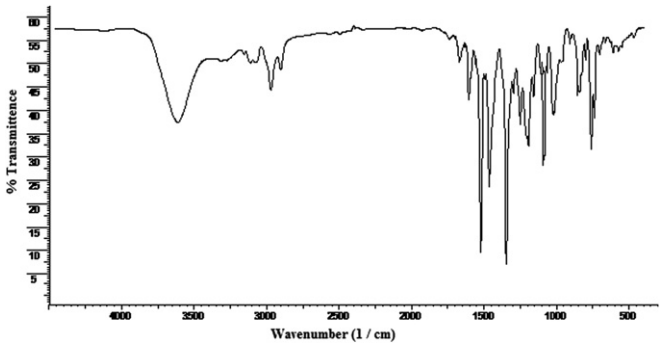


Fig. 4. IR spectra of dye **6b**.

J = 13.2 Hz, Ar–CH_2–Ar), 4.20 (6H, s, Ar–OCH_3), 5.22 (4H, s, CH_2), 7.30 and 7.72 (2H, s, OH), 7.26–8.25 (26H, m, Ar–H), 9.72 (1H, broad, NH), 10.42 (1H, broad, NH), MS m/z (M^+): 1178.

*2.2.2.8. 25,227-bis-[(4-nitrobenzyloxy-26,28-dihydroxy-5,17-[3′-methyl-4′(3″-chloro phenylazo-1′-H-pyrazole-5′-ylazo]calix[4]arene (**6h**).* Golden yellow solid, yield 1.47 g (75%), m.p: 220 °C. Anal. Cal. for $C_{62}H_{48}N_{14}O_8Cl_2$; C: 62.68%; H: 4.04%; N: 16.51%; Found: C: 62.71%; H: 4.08%; N: 16.57%. IR (KBr) υ (cm^{-1}): 3529 cm^{-1} (–OH), 3018–3036 cm^{-1} (Aromatic C–H), 2940–2963 cm^{-1} (Aliphatic C–H), 1578 cm^{-1} (N=N), 1097 cm^{-1} (C–O). ^{1}H NMR (DMSO-d_6, 25 °C) δ (ppm): 2.93, 3.23 (6H, s, pyrazole–CH_3), 3.51 and 4.25 (8H, d, J = 13.2 Hz, Ar–CH_2–Ar), 5.23 (4H, s, CH_2), 7.25 and 7.70 (2H, s, OH), 7.23–8.19 (26H, m, Ar–H), 10.05 (1H, broad, NH), 11.85 (1H, broad, NH). MS m/z (M^+): 1187.

*2.2.2.9. 25,27-bis-[(4-nitrobenzyloxy-26,28-dihydroxy-5,17-[3′-methyl-4′(3″-methyl phenylazo-1′-H-pyrazole-5′-ylazo]calix[4]arene (**6i**).* Yellow-brown solid, yield 0.75 g (65%), m.p: 230 °C. Anal. Cal. for $C_{64}H_{54}N_{14}O_8$; C: 67.01%; H: 4.71%; N: 17.10%; Found: C: 67.06%; H: 4.75%; N: 17.14%. IR (KBr) υ (cm^{-1}): 3526 cm^{-1} (–OH), 3015–3032 cm^{-1} (Aromatic C–H), 2948–2964 cm^{-1} (Aliphatic C–H), 1580 cm^{-1} (N=N), 1093 cm^{-1} (C–O). ^{1}H NMR (DMSO-d_6, 25 °C) δ (ppm): 2.87, 3.16 (6H, s, pyrazole–CH_3), 3.50 and 4.28 (8H, d, J = 13.2 Hz, Ar–CH_2–Ar), 4.05 (6H, s, Ar–CH_3), 5.17 (4H, s, CH_2), 7.22 and 7.67 (2H, s, OH), 7.22–8.20 (26H, m, Ar–H), 9.76 (1H, broad, NH), 10.65 (1H, broad, NH). MS m/z (M^+): 1146.

*2.2.2.10. 25,27-bis-[(4-nitrobenzyloxy-26,28-dihydroxy-5,17-[3′-methyl-4′(4″-nitro phenylazo-1′-H-pyrazole-5′-ylazo]calix[4]arene (**6j**).* Dark brown solid, yield 0.95 g (79%), m.p: 150 °C. Anal. Cal. for $C_{62}H_{48}N_{16}O_{12}$; C: 61.59%; H: 3.97%; N: 18.54%; Found: C: 61.62%; H: 3.95%; N: 18.57%. IR (KBr) υ (cm^{-1}): 3526 cm^{-1} (–OH), 3012–3037 cm^{-1} (Aromatic C–H), 2950–2965 cm^{-1} (Aliphatic C–H), 1578 cm^{-1} (N=N), 1522 cm^{-1} (NO_2), 1094 cm^{-1} (C–O). ^{1}H NMR (DMSO-d_6, 25 °C) δ (ppm): 2.92, 3.22 (6H, s, pyrazole–CH_3), 3.45 and 4.25 (8H, d, J = 13.2 Hz, Ar–CH_2–Ar), 5.21 (4H, s, CH_2), 7.25 and 7.68 (1H, s, OH), 7.21–8.21 (26H, m, Ar–H), 9.98 (1H, broad, NH), 10.60 (1H, broad, NH). MS m/z (M^+): 1208.

*2.2.2.11. 25,27-bis-[(4-nitrobenzyloxy-26,28-dihydroxy-5,17-[3′-methyl-4′(4″-methoxy phenylazo-1′-H-pyrazole-5′-ylazo]calix[4] arene (**6k**).* Dark brown solid, yield 0.88 g (75%), m.p: 142 °C. Anal. Cal. for $C_{64}H_{54}N_{14}O_{10}$; C: 65.19%; H: 4.58%; N: 16.63%; Found: C: 65.24%; H: 4.55%; N: 16.60%. IR (KBr) υ (cm^{-1}): 3528 cm^{-1} (–OH), 3016–3035 cm^{-1} (Aromatic C–H), 2951–2970 cm^{-1} (Aliphatic C–H), 1575 cm^{-1} (N=N), 1097 cm^{-1} (C–O). ^{1}H NMR (DMSO-d_6, 25 °C) δ (ppm): 2.89, 3.21 (6H, s, pyrazole–CH_3), 3.49 and 4.21 (8H, d, J = 13.2 Hz, Ar–CH_2–Ar), 4.18 (6H, s, Ar–OCH_3), 5.25 (4H, s, CH_2), 7.20 and 7.70 (2H, s, OH), 7.10–8.18 (26H, m, Ar–H), 9.95 (1H, broad, NH), 10.58(1H, broad, NH). MS m/z (M^+): 1176.

*2.2.2.12. 25,27-bis-[(4-nitrobenzyloxy-26,28-dihydroxy-5,17-[3′-methyl-4′(4″-chloro phenylazo-1′-H-pyrazole-5′-ylazo]calix[4]arene (**6l**).* Brown solid, yield 0.92 g (78%), m.p: 143 °C. Anal. Cal. for $C_{62}H_{48}N_{14}O_8Cl_2$; C: 62.68%; H: 4.04%; N: 16.51%; Found: C: 62.72%; H: 4.07%; N: 16.55%. IR (KBr) υ (cm^{-1}): 3528 cm^{-1} (–OH), 3015–3028 cm^{-1} (Aromatic C–H), 2945–2966 cm^{-1} (Aliphatic C–H), 1578 cm^{-1} (N=N), 1096 cm^{-1} (C–O). ^{1}H NMR (DMSO-d_6, 25 °C) δ (ppm): 2.86, 3.20 (6H, s, pyrazole–CH_3), 3.48 and 4.22 (8H, d, J = 13.2 Hz, Ar–CH_2–Ar), 5.26 (4H, s, CH_2), 7.24 and 7.67 (2H, s, OH), 7.15–8.20 (26H, m, Ar–H), 10.11 (1H, broad, NH), 12.25 (1H, broad, NH). MS m/z (M^+): 1187.

*2.2.2.13. 25,27-bis-[(4-nitrobenzyloxy-26,28-dihydroxy-5,17-[3′-methyl-4′(4″-methyl phenylazo-1′-H-pyrazole-5′-ylazo]calix[4]arene (**6m**).* Light brown solid, yield 0.85 g (75%), m.p: 123 °C. Anal. Cal. for $C_{64}H_{54}N_{14}O_8$; C: 67.01%; H: 4.71%; N: 17.10%; Found: C: 67.05%; H: 4.72%; N: 17.13%. IR (KBr) υ (cm^{-1}): 3527 cm^{-1} (–OH), 3016–3030 cm^{-1} (Aromatic C–H), 2942–2963 cm^{-1} (Aliphatic C–H), 1576 cm^{-1} (N=N), 1095 cm^{-1} (C–O). ^{1}H NMR (DMSO-d_6, 25 °C) δ (ppm): 2.85, 3.24 (6H, s, pyrazole–CH_3), 3.49 and 4.25 (8H, d, J = 13.2 Hz, Ar–CH_2–Ar), 4.06 (6H, s, Ar–CH_3), 5.24 (4H, s, CH_2), 7.23 and 7.68 (1H, s, OH), 7.20–8.22 (26H, m, Ar–H), 9.92 (1H, broad, NH), 10.60 (1H, broad, NH). MS m/z (M^+): 1146.

3. Results and discussion

In our earlier studies, carbocyclic and heterocyclic amine substituted azocalix[4]arenes [36–39] were investigated. In this

Table 1
Influence of solvent on λ_{max} (nm) of dyes **6(a–m)**.

Dye no.	DMSO	DMF	Acetonitrile	Methanol	Acetic acid	Chloroform
6a	388	396	323	327,408s	326,409s	325,409s
6b	357s, 521	356,430, 518	354s, 410	351s, 418	352s, 412	351s, 415
6c	349,425s	346,426s	344, 426	344,423s	344,427s	346,422s
6d	338,410s	336,416s	334,406s	333,401s	333,413s	334,414s
6e	344,409s	336,419	338,410	340,413	338,416	342,418
6f	346,400s	344,410	344,393s	342s,388	340s,393	347,386s
6g	414	416	406	324,416s	320,415s	415
6h	334,408s	333,408s	330,390s	330,388s	330,404s	330,405s
6i	400	332,416s	331,405s	333,410s	331,415s	332,414s
6j	340	340,566s	332,404s	336	334,410s	338,422s
6k	408	376	406	446	352,425s	386
6l	338,556s	339,561s	336,414s	340,535s	346,420s	340,418s
6m	344	364,564s	338	334	324,387s	384

s: shoulder.

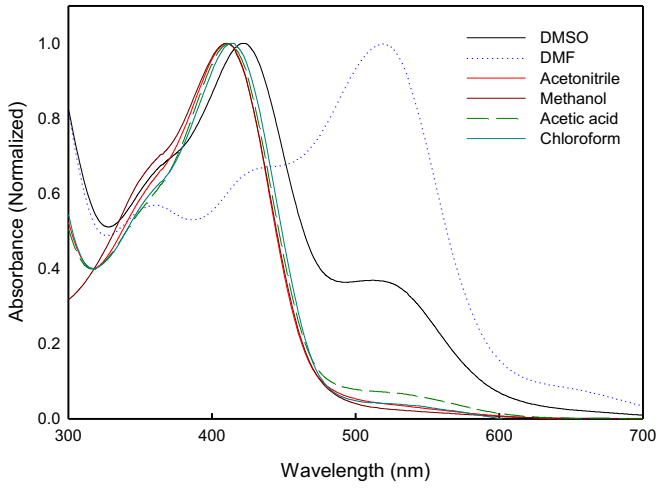


Fig. 5. Absorption spectra of dye **6b** in various solvents.

paper, the synthesis of some tetrakisazocalix[4]arene derivatives **6(a–m)** have been reported. The compounds of thirteen new hetaryltetrakisazocalix[4]arenes **6(a–m)** were prepared by coupling 25,27-bis-(4-nitrobenzyloxy)-26,28-dihydroxycalix[4]arene with diazotized heterocyclic amines **2(a–m)** in nitrosylsulphuric acid. firstly, *p-tert*-butylcalix[4]arene was prepared by

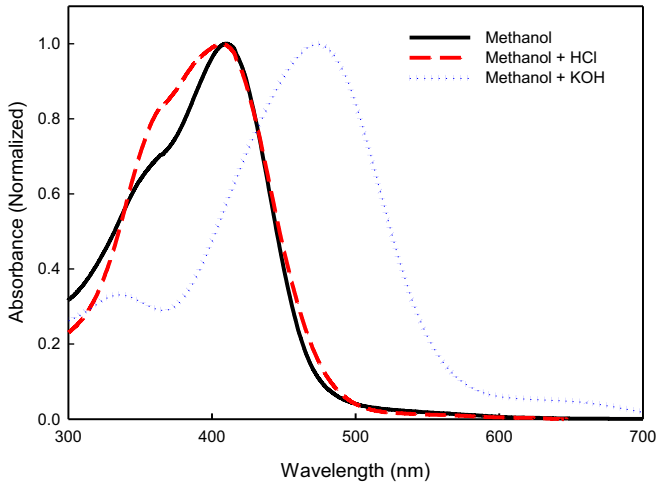


Fig. 6. Absorption spectra of dye **6b** in acidic and basic solutions.

reaction of *p-tert*-butylphenol with formaldehyde according to the method given in reported literature [42]. Secondly, the calix[4]arene was obtained from treatment of *p-tert*-butylcalix[4]arene with aluminium chloride according to the method given in literature [43]. At the third stage, 25,27-bis-(4-nitrobenzyloxy)-26,28-dihydroxycalix[4]arene was synthesized according to the procedures given in literature [44]. Afterwards, we synthesized 2-arylhydrazone-3-ketiminobutyronitriles **1(a–m)** and 5-amino-4-arylazo-3-methyl-1-H-pyrazoles **2(a–m)** according to the procedures given in literature [14–22]. The heterocyclic diazonium salts were derived from heterocyclic amines **2(a–m)**. Later, 2.0 equivalent heterocyclic diazonium salts **2(a–m)** reacted with 1.0 equivalent of 25,27-bis-(4-nitrobenzyloxy)-26,28-dihydroxycalix[4]arene in DMF/MeOH mixture to obtain the corresponding hetaryltetrakisazocalix[4]arene derivatives **6(a–m)**. These general reactions are shown in Figs. 1 and 2. By the purification of the reaction mixtures, the thirteen hetaryltetrakisazocalix[4]arene derivatives have been obtained in 62–79% yield.

The obtained products from the above mentioned reactions were characterized using elemental analysis, Mass, FT-IR and ^{1}H NMR spectral data. The hetaryltetrakisazocalix[4]arene derivatives **6(a–m)** may exist in five possible tautomeric forms which are a phenol-azo form, a phenol-hydrazone form, two quinone-hydrazone forms, and quinone form named A, B, C, D and E, respectively, as shown in Fig. 3. The infrared spectra of all the compounds **6(a–m)** showed a band in the range of 3520–3529 cm^{-1} corresponding to ν_{OH} and a band located at 3010–3037 cm^{-1} assigned to aromatic C–H. The others ν_{max} values at 2940–2970 cm^{-1} aliphatic C–H, 1521–1424 cm^{-1} (NO_2), 1575–1582 cm^{-1} (N=N), 1090–1097 cm^{-1} (C–O) were also recorded. Because of the infrared spectra of all compounds showed –OH bands at 3520–3529 cm^{-1} and (C–O) bands 1090–1097 cm^{-1}, it can be suggested that these compounds do not exist as the keto forms in **C**, **D** and **E** in the solid state.

The IR spectra of dye **6b** is shown in Fig. 4.

The structures of **6(a–m)** were examined by using high-resolution NMR. The ^{1}H NMR spectrums were measured in DMSO-d_6 at 25 °C. The ^{1}H NMR spectra of all compounds have typical AB patterns and showed four doublet peak for methylene protons ($ArCH_2Ar$) at between 3.45 and 4.28 ppm. The **6a**, **6b**, **6d**, **6f**, **6h**, **6j**, **6l** showed two singlet peak for methyl protons (pyrazole–CH_3) at between 2.85–2.98 and 3.10–3.24 ppm. The **6c**, **6e**, **6g**, **6i**, **6k**, **6m** showed two singlet peak for methyl protons ($Ar–OCH_3$) and ($Ar–CH_3$) at between 4.10-4.20 ppm and 4.05–4.07 ppm. All compounds **6(a–m)** showed a multiplet peak at between 7.10 and 8.25 ppm for aromatic protons (Ar–H), a singlet peak at between 7.20 and 7.72 ppm for hydroxyl proton (–OH). The ^{1}H NMR spectrums of dyes **6(b–f)**, **6h** and **6l** showed a broad peak at between

Table 2
Absorption maxima of dyes **6(a–m)** in acidic and basic solutions.

Dye no.	Methanol	Methanol + KOH	Methanol + HCl	Chloroform	Acetic acid
6a	327,408s	375	326,411s	325,409s	326,409s
6b	351s, 418	310s, 475,	353s, 409	351s, 415	352s, 412
6c	344,423s	376,421s	343,433s	346,422s	344,427s
6d	333,401s	388,304s	333,412s	334,414s	333,413s
6e	340,413	373,313s	338,423s	342,418	338,416
6f	342s,388	388,422s	348,417s	347,386s	340s,393
6g	324,416s	382,422s	320,415s	415	320,415s
6h	330,388s	387,419s	331,401s	330,405s	330,404s
6i	333,410s	377,405s	331,415	332,414s	331,415s
6j	336	371,540s	345,422s	338,422s	334,410s
6k	446	364	360,430s	386	352,425s
6l	340,535	368,522s	340,430s	340,418s	346,420s
6m	334	369	340	384	324,387s

s: shoulder.

9.72 and 10.21 ppm for (–NH) proton and a broad peak at 11.20–12.35 ppm for tautomeric hydrazo (–NH) proton. The ^{1}H NMR spectra of dyes **6a**, **6g**, **6i**, **6j**, **6k** and **6m** showed only NH proton, but did not showed hydrazo NH proton. According to ^{1}H NMR results, dyes named as **6a**, **6g**, **6i**, **6j**, **6k** and **6m** have a mixture of phenol-azo (**A**) and quinone (**E**) tautomeric forms, but not phenol-hydrazone (**B**), quinone-hydrazone (**C**, **D**) tautomeric form. The dyes named as **6(b–f)**, **6h** and **6l** present as a mixture of **B**, **C** and **D** three tautomeric forms in DMSO-d_6 as showed in Fig. 3.

3.1. UV–visible analysis

In general, tautomeric equilibrium strongly depend 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 **6(a–m)** were measured in various solvents at a concentration of approximately (10^{-6}–10^{-8} M). Solvents used for the UV 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) [45]. The results obtained from the absorption measurements are given in Table 1. The visible absorption spectra of the dyes did not have correlation with the polarity of solvents. Only plausible explanation for this irregular behaviour 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 [46]. Similar behaviours have been reported for azocaliks[4]arene, azocaliks[6]arene, azoresorsinarene and azoindole and this solvent independent manner of the absorption maxima had been explained by the stability in molecules [38,39,45,47]. 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 [46]. 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 **6b** in various solvents are depicted in Figs. 5 and 6, respectively.

There is no significant change in the absorption spectra of the dyes in methanol, acetic acid and chloroform except for dye **6e**, **6f**, **6g**, **6j**, **6k**, **6l**, **6m**.

It was observed that λ_{max} of the dyes shifted hypsochromically in acetic acid with respect to the λ_{max} in methanol except for dyes **6b**, **6f** and **6l**. λ_{max} values of dyes in DMSO and DMF were shifted bathochromically with respect to the λ_{max} in methanol except for **6k** and **6l**. λ_{max} values of dyes in DMF were shifted bathochromically with respect to the λ_{max} in methanol except for **6e** and **6i**. For example; the absorption maxima of **6b** was observed at 412 nm in acetic acid, 521 nm in DMSO, 518 nm in DMF and 418 nm in methanol, respectively (Fig. 5).

The λ_{max} of dyes **6c**, **6d**, **6e**, and **6f** did not change significantly in the all solvents used for the absorption measurements. The absorption spectra of prepared dyes showed a maximum absorption peak with a shoulder in all solvents except for **6a**, **6g**, **6i**, **6j**, **6k** and **6m**. The dye **6a** in methanol, acetic acid and chloroform, **6g** in methanol and acetic acid, **6j** except for methanol and DMSO in all solvent, **6k** in acetic acid, **6m** in DMF and acetic acid showed a maximum absorption peak with a shoulder. It suggest that these dyes present more than one tautomeric form. Typical examples of these results are given in Fig. 5.

The effects of the acid and base on the absorption spectrum of the dyes solutions were investigated and the result were depicted in Table 2.

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 **6(a–m)** showed a bathochromic shifts with the addition of base to methanol except for **6f** and **6k**. For example; λ_{max} of **6b** was recorded at 418 nm in methanol, 475 nm in methanol + KOH (Fig. 6).

When hydrochloric acid (0.1 M) was added to the dye solutions in methanol, hypsochromic shifts were detected, except for **6h**, **6j** and **6m**. The λ_{max} of **6b** was observed at 418 nm in methanol and 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. 6).

As seen in Table 1 accommodation of electron-withdrawing and electron donating groups into the benzene ring resulted in bathochromically shifts in acetonitrile, methanol and chloroform except for **6g**, acetic acid except for **6g**, **6m** when compared with dye **2a**. In contrast, introduction of electron-withdrawing and electron donating groups into the benzene ring gave rise to hypsochromic shifts in DMSO except for **6b**, **6g**, **6i**, **6k**, in DMF except for **6b**, **6e**, **6f**, **6g**, **6k** when compared with dye **2a**. The introduction of nitro groups into the benzene ring resulted in large bathochromic shift o- and m-position and small bathochromic shift in p-position in all solvent (For dye **6b** $\Delta\lambda$: 89 nm, for dye **6f** $\Delta\lambda$: 61 nm, for dye **6j** $\Delta\lambda$: 9 nm relative dye **6a** for spectra in methanol). Moreover, the absorption spectra of methoxy derivatives (dye **6c**) gave rise to bathochromic shift in all solvent except for DMSO and DMF, dye **6g** except for methanol and acetic acid, dye **6k** except for DMF.

4. Conclusions

In summary, the synthesis and characterization of thirteen novel hetaryltetrakisazocalix[4]arene based dyes **6(a–m)** were studied by means of FT-IR, ^{1}H NMR and Mass spectroscopic techniques as well as Elemental Analysis. The heterocyclic diazonium salts were derived from heterocyclic amines **2(a–m)** in nitrosylsulphuric acid, and reacted with 0.5 equivalent of 25,27-bis-(4-nitrobenzyloxy)-26,28-dihydroxycalix[4]arene in DMF/MeOH mixture (26 mL, 8:5, v/v) to afford 25,27-bis-[(4-nitrobenzyloxy-26,28-dihydroxy-5,17-bis-[3′-methyl-4′-arylylazo-1′-H-pyrazole-5′-ylazo]calix[4]arene **6(a–m)**. The FT-IR spectra results of hetaryltetrakisazocalix[4]arene dyes **6(a–m)** revealed that these compounds exist in forming phenol-azo and phenol-hydrazone form (**A**, **B**) in solid state. The results of ^{1}H NMR spectra of the dyes for **6a**, **6g**, **6i**, **6j**, **6k** and **6m** have a mixture of phenol-azo (**A**) and quinone (**E**) tautomeric forms, but not phenol-hydrazone (**B**), quinone-hydrazone (**C**, **D**) tautomeric form. The dyes **6(b–f)**, **6h** and **6l** present as a mixture of **B**, **C** and **D** three tautomeric forms. The ^{1}H NMR spectrum of all compounds have typical AB patterns and showed four doublet peak for methylene protons ($ArCH_2Ar$) at between 3.45 and 4.28 ppm. According to these results, it can be said that all compounds have cone conformation.

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