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Synthesis of New Thiacalix[4]arene Based Azo Dyes and Analysis of Absorption Spectrums

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ABSTRACT

In this study, firstly a novel thiacalix[4]arene functionalized from the phenolic oxygen side was synthesized. Then, a series of dyes were synthesized by linking the heterocyclic groups to the novel thiacalix[4]aren through a diazotization reaction. The azo dyes were characterized by UV-Vis, FT-IR and ^{1}H-NMR spectroscopic techniques. Furthermore, effect of solvent and acid-base upon the absorption spectra of the azo dyes were investigated.

ÖZ

Anahtar Kelimeler:
Azo Boyaları,
Azo Tiyakaliksaren

Bu çalışmada ilk olarak fenolik oksijen tarafından işlevselleştirilmiş yeni bir tiakaliks [4] aren sentezlendi. Daha sonra, heterosiklik grupların, tiyakaliks[4]arene diazolama reaksiyonu yoluyla bağlanarak, bir seri boya sentezlendi. Azo boyaları UV-Vis, FT-IR ve 1H-NMR spektroskopik teknikleri ile karakterize edildi. Ayrıca, azo boyaların absorpsiyon spektrumları üzerine çözücü ve asit baz etkisi araştırıldı.

1. Introduction

Being half of the dyes used in textiles, Azo dyes have been known for many years. In recent years, it has been reported that dyes obtained by the use of heterocyclic compounds exhibit very good light, washing, and bleaching fastness related to yellow-orange color range. There are many examples related with the synthesis of heteroaryl azo dyes and their usage as a dyestuff for synthetic fabrics [1-5].

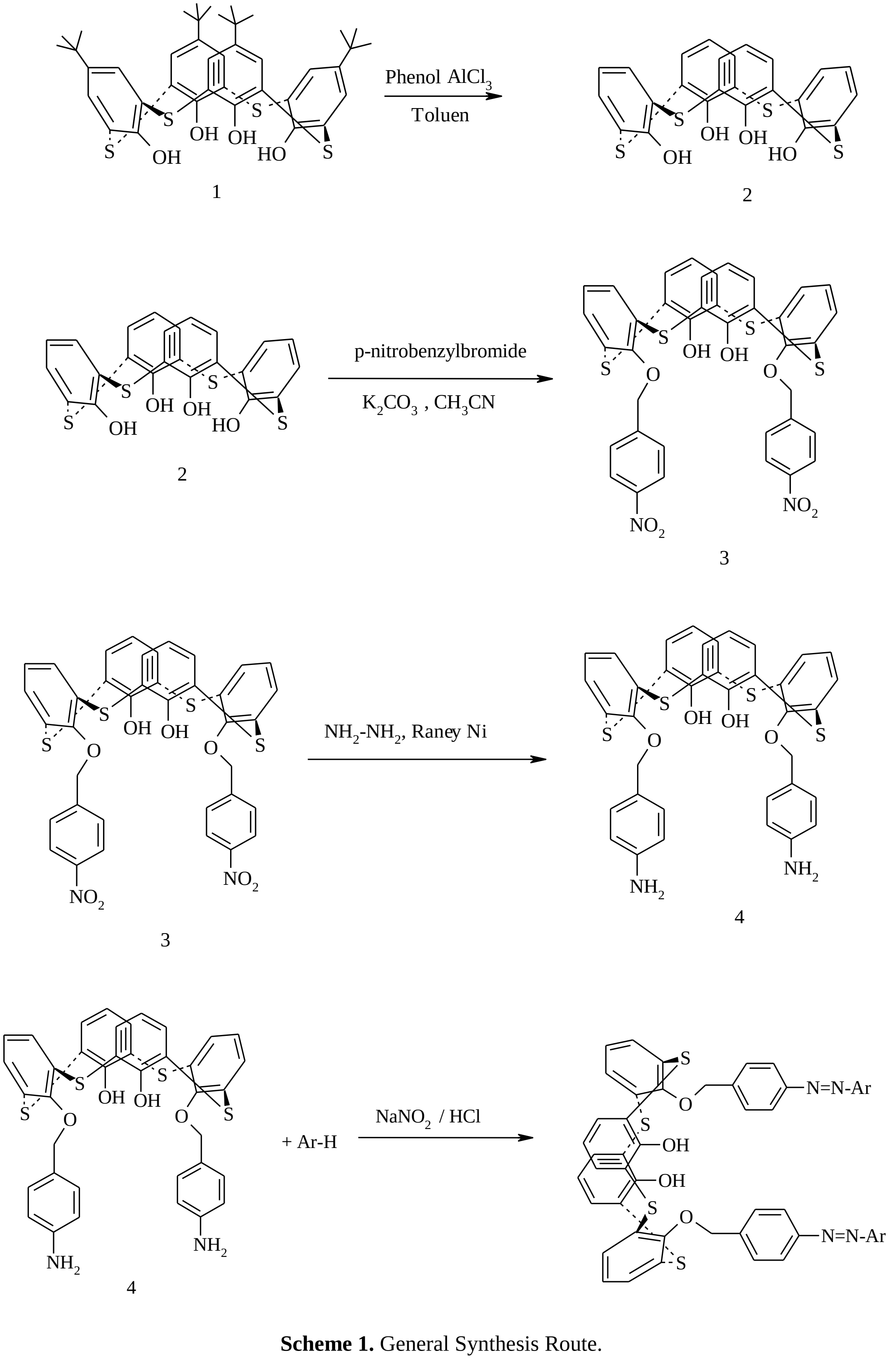
Within the macrocyclic compounds family, calixarene derivatives have also been synthesized in the field of heterocyclic dyes because of that azo groups make a significant chromogenic contribution to calixarenes [6-7]. The modification of the calix skeleton involve rearrangement through the methylene bridges among the phenol units by heteroatoms such as nitrogen, oxygen, sulfur [8]. Sone et al. synthesized p-*tert*-butylthiacalix[4]arene for the first time, in which sulfur are replaced to CH_2 groups of p-*tert*-butylcalix[4]arene [9-10]. It was reported that oxidation of bridging sulfur afforded sulfinyl- and sulfonylcalix arenes, which showed intrinsic metal ion selectivity determined by the hardness and softness of the ion [11]. Furthermore, thiacalixarenes are applied to many fields such as molecule/ion Carrier [12], catalyzer [13], electrode [14], liquid membrane [15], sensor [16]. Morever, the dyes derived from thiacalixarene are also available for other purposes in the literature. For example; thiacalixarene diazonium salts were converted to *p*-azo-thiacalixarene derivatives at room temperature with high yield. At the same time, the study claimed that tetra-amine-derived thiacalixarene can be obtained through reduction at the *p*-position [17]. In another comprehensive study, the acyloin and heteroaryl azo derivatives of the thiacalix[4]arene were synthesized and the properties of the cations were examined [18].

Studies to date show that future studies will be based on the functioning of the azothiacalix[4]arene, which is a subclass of calix[n]arenes. In particular, host-guest interaction with metal ions will facilitate the use of these compounds as sensors and electrodes. For all these reasons, in this study, a novel thiacalix[4]aren functionalized from the phenolic oxygen side was synthesized at the first stage. Then, a series of dyes were synthesized by linking the heterocyclic groups to the novel thiacalix[4]aren through a diazo reaction. The azo dyes were characterized by UV-vis, FT-IR and ^{1}H-NMR spectroscopic techniques.

2. Material and Methods

The used devices are as follows: Evaporator (Heidolph 4000 Efficient), melting point device (Stuart SMP-30), oven (NFe FN-120), balance (Radwag AS-220), mantle heater (Thermo Scientific), magnetic stirrer (VELP Scientifica). UV-vis measurements and FT-IR analyzes of the synthesized compounds were performed using Shimadzu UV-1601 UV-visible and Perkin Elmer FT-IR spectrophotometers. ^{1}H-NMR spectra were taken with Bruker Ultra Shield Plus 400 MHz. The chemicals were obtained from high purity Merck, and Sigma-Aldrich brands.

In this study, *p*-tert-butylthiacalix[4]arene (1) was synthesized in accordance with the literature [19]. Thiacalix[4]arene (2) was obtained by eliminating the tertiary butyl groups of this compound [12]. The compound was then reacted with *p*-nitrobenzylbromide to obtain 25,27-bis-(4-nitrobenzyloxy)-26,28- thiacalix[4]arene (3). The nitro groups on this compound were reduced and 25,27-bis-(4-aminobenzyloxy)-26,28- dithiacalix[4]arene (4) was producted. This compound was reacted with a series of coupling compounds to obtain the new azothiacalix[4]arene derivatives **(Scheme 1)**.

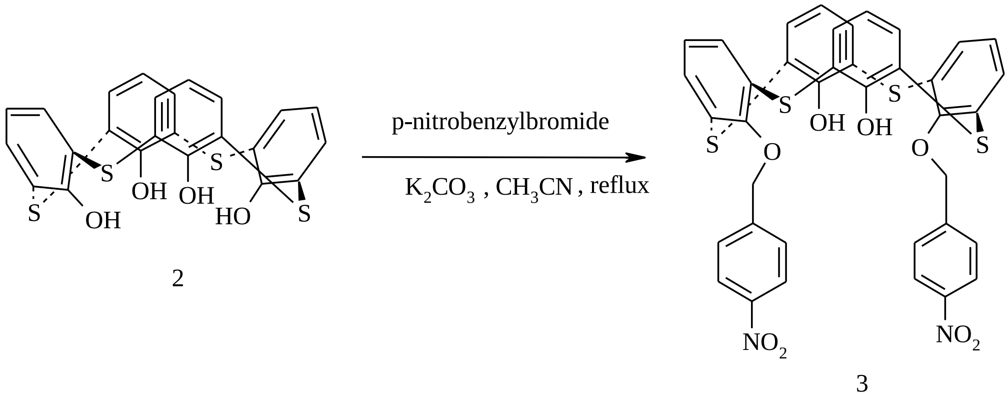


Scheme 1. General Synthesis Route.

Synthesis of 25,27-bis-(4-nitrobenzyloxy)-26,28 dihydroxythiacycline [4]arene (3)

A 500 mL two necked flask was charged with a reaction mixture of 2.756 g (5.55 mmol) of thiacalix [4] arene, 0.767 g (5.55 mmol) of K_2CO_3 and 300 mL of acetonitrile and heated for 30 minutes. 2,398 g (11,1 mmol) of *p*-nitrobenzylbromide was added to the reaction mixture and boiled for 24 hours. The white reaction mixture is taken up in the evaporator and the solvent is evaporated. 1 N 100 mL HCl is added and a suspension is obtained. The insoluble material was removed by filtration and washed sequentially with methanol and distilled water. The dried material is crystallized from chloroform **(Scheme 2).**

Yield: 2,05 g, 48%; **mp:** 225 ºC **FT-IR,** ν_{max} (cm^{-1}): 3385(-OH); 3060 (Arom.C-H); 2950 (Aliphatic C-H); 1512,1346 ($-NO_2$); 1001 (C-O) ^{1}H-NMR (DMSO-d_6), δ(ppm): 5,51 (s, 4H, $-CH_2$); 6,81, 7,09, 7,79 (m, 12H, calix aromatic C-H); 7,61, 8,21 (d, 8H, Arom.C-H); 7,88 (s, 2H, -OH).

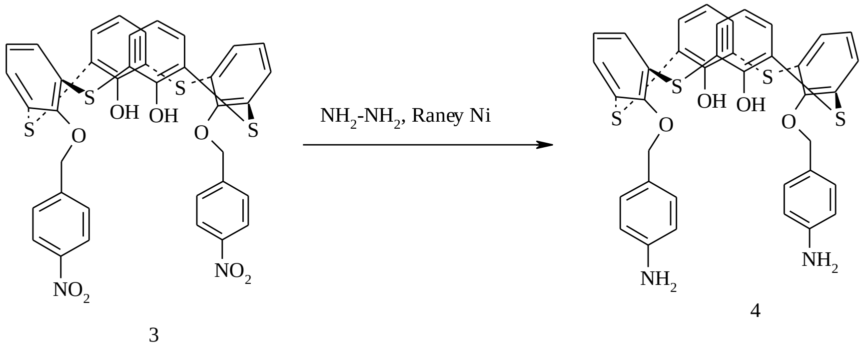


Scheme 2. Synthesis of *25,27-bis*-(4-nitrobenzyloxy)-26,28-dihydroxythiacalix[4]arene

Synthesis of 25,27-bis-(4-aminobenzyloxy)-26,28-dihydroxythiacalix[4]arene (4)

2.02 g (2.64 mmol) of 25,27-bis-(4-nitrobenzyloxy)-26,28-dihydroxythiacalix[4]arene, 2.87 g of Raney Nickel, 130 mL of ethanol and 260 mL of THF were added to a 500 mL flask, 5,33 mL of $N_2H_4.H_2O$ was added slowly to the stirred flask at room temperature. After boiling for 12 hours, 2.66 mL of $N_2H_4.H_2O$ was slowly added dropwise to the green mixture and the color turned blue. After further boiling for 24 hours, the green reaction mixture is cooled and filtered through bilayer filter paper. The green material is crystallized from chloroform **(Scheme 3)**.

Yield: 1.242 g, 67%; **mp:** 330 ºC (decomp.) **FT-IR,** ν_{max} (cm^{-1}): 3423 (-OH); 3325 ($-NH_2$); 3007 (Arom. C-H); 2919 (Aliphatic C-H); 1066 (C-O) ^{1}H-NMR (DMSO-d_6), δ(ppm): 3,82, 5,26 (s, 4H, $-CH_2$); 6,20, 8,75 (m, 20 H, Arom.C-H); 11,25 (s, 2H, -OH); 13,01, 15,05 (s, 4H, $-NH_2$).

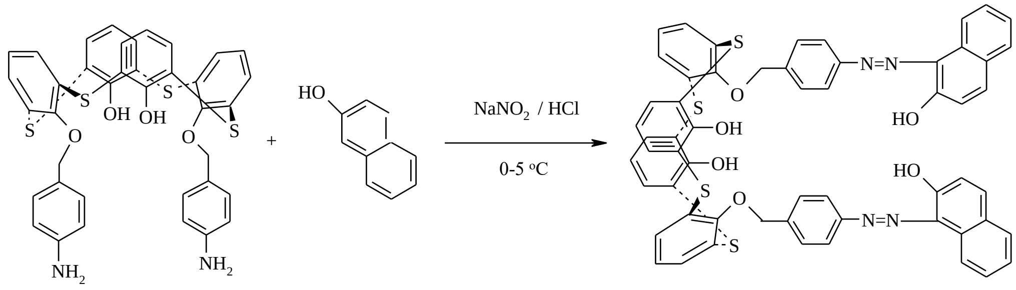


Scheme 3. Synthesis of 25,27-bis- (4-aminobenzyloxy) -26,28-dihydroxy-thiacalix[4]arene compound.

Synthesis of 25,27-bis-[4- (2'-hydroxynaphthol-1-yl-azo) benzyloxy]-26,28-dihydroxy thiacalix[4]arene (4a)

0,1 g (0.14 mmol) of 25,27-bis- (4-aminobenzyloxy)-26,28 dihydroxythiacalix[4]arene dissolved in DMF and 0.2 mL of HCl were added in an ice-water bath. In another beaker, a solution of 0.022g (0.35mmol) $NaNO_2$ with the lowest possible water was added dropwise to the reaction mixture in an ice water bath and stirred for 2 hours. On the other hand, a basic solution of 0.40 g (0.28 mmol) of 2-naphthol, for using as a coupling component, with NaOH, was prepared and added dropwise to the beaker from which the diazonium salt was prepared. Stir in ice-water bath for 2 hours. After this time, saturated sodium acetate solution was added to add the mixture to pH = 7 and pure water was added. The precipitate formed was filtered and dried. The red material was crystallized from DMSO **(Scheme 4).**

Yield: 0,102 g, 70,9%; **mp:** 230-240 ºC **FT-IR,** ν_{max} (cm^{-1}): 3266 (-OH); 3060 (Arom.C-H); 2923 (Aliphatic C-H); 1678, 1596 (N=N); 1090 (C-O). ^{1}H-NMR (DMSO-d_6), δ(ppm): 4.76-4.80 (s, 4H, -CH_2); 6.61-8.81 (m, 32H, Arom.C-H); 11.20, (s, 2H, -OH); 9.80 (s, 2H, -OH).



4

4a

Scheme 4. Synthesis of 25,27-bis-[4-(2-hydroxy-butanol-1-yl-azo) benzyloxy]-26,28-dihydroxy thiacalix[4]arene **(4a).**

Other compounds **(4b-4h**) in the study were also synthesized according to this procedure (**Scheme 5**).

Synthesis of 25,27-bis-[4-(2 ', 4'-dihydroxyquinolin-3'-yl-azo) benzyloxy]-2,28-dihydroxy thiacalix[4]arene (4b)

Yield: 0,076 g, **51,1%; mp:** 280-290 ºC **FT-IR,** ν_{max} (cm^{-1}): 3264 (-OH); 3059 (Arom.C-H); 2926 (Aliphatic C-H); 1678, 1596 (N=N); 1090 (C-O). ^{1}H-NMR (DMSO-d_6), δ(ppm): 4.91 (s, 4H, -CH_2); 7.05-8.94 (m, 28H, Arom.C-H); 11.65 (s, 2H, -OH) , 9.90(s, 2H, -OH).

Synthesis of 25,27-bis-[4- (8'-hydroxyquinolin-7'-yl-azo) benzyloxy]-26,28-dihydroxy thiacalix[4]arene (4c)

Yield: 0,087 g, **60,3%; mp:** 280-288 ºC **FT-IR,** ν_{max} (cm^{-1}): 3268 (-OH); 3064 (Arom.C-H); 2926 (Aliphatic C-H); 1678, 1607 (N=N); 1090 (C-O). ^{1}H-NMR (DMSO-d_6), δ(ppm): 4.90 (s, 4H, -CH_2); 7.14-8.84 (m, 30H, Arom.C-H); 11.05 (s, 2H, -OH), 9.80(s, 2H, -OH).

Synthesis of 25,27-bis-[4-(4'-hydroxy-coumarin-3-yl-azo) benzyloxy]-26,28-dihydroxy thiacalix[4]arene (4d)

Yield: 0,065 g, **43,6%; mp:** 275-285 ºC **FT-IR,** ν_{max} (cm^{-1}): 3267 (-OH); 3059 (Arom.C-H); 2926 (Aliphatik C-H); 1678, 1607 (N=N); 1090 (C-O). ^{1}H-NMR (DMSO-d_6), δ(ppm): 4.88 (s, 4H, -CH_2); 7.12-8.89 (m, 28H, Arom.C-H); 12.85 (s, 2H, -OH), 11.10 (s, 2H, -OH).

Synthesis of 25,27-bis-[4-(7'-hydroxy-4'-methylcoumarin-8'-yl-azo)benzyloxy]-26,28- dihyroxythiacalix[4] arene (4e)

Yield: 0,050 g, **32,7%; mp:** 295-300 ºC **FT-IR,** ν_{max} (cm^{-1}): 3266 (-OH); 3059 (Arom.C-H); 2926 (Aliphatic C-H); 1678, 1597 (N=N); 1090 (C-O). ^{1}H-NMR (DMSO-d_6), δ(ppm): 6.18 (s, 2H, -CH); 4.91 (s, 4H, -CH_2); 7.05-9.06 (m, 24H, Arom.C-H); 11.10 (s, 2H, -OH) , 10.05 (s, 2H, -OH).

Synthesis of 25,27-bis- [4-(3-methyl-5'-pyrazolon-4-yl-azo) benzyloxy]-26,28-dihyroxythiacalix[4]arene (4f)

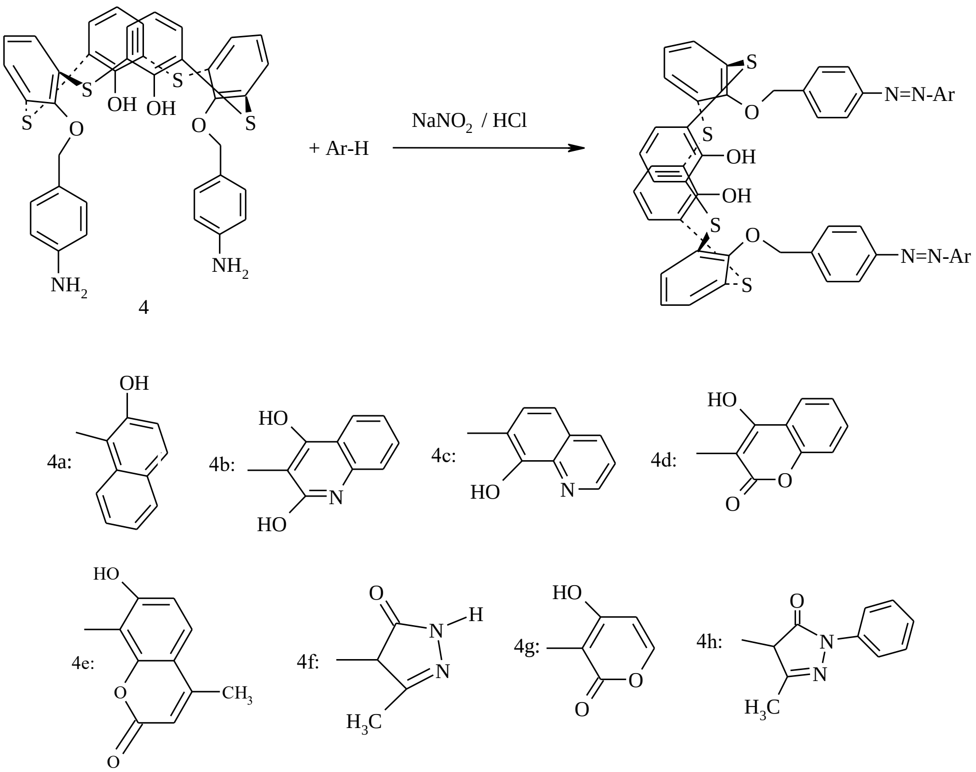
Yield: 0,052 g, **39,7%; mp:** 285-295 ºC, **FT-IR,** ν_{max} (cm^{-1}): 3265 (-OH); 3059 (Arom.C-H); 2922 (Aliphatic C-H); 1677(N=N); 1090 (C-O). ^{1}H-NMR (DMSO-d_6), δ(ppm): 4.79 (s, 4H, -CH_2); 2.25 (s, 6H, -CH_3); 6.50-8.15 (m, 20H, Arom.C-H); 8.15 (s, 2H, -OH); 9.57 (s, 1H, -NH).

Synthesis of 25,27-bis-[4-(4'-hydroxy-6'-methyl-2-pyrid-3-yl-azo)benzyloxy]-26,28- dihyroxythiacalix[4]arene (4 g)

Yield: 0,049 g, **35,3%; mp:** 292-307 ºC **FT-IR,** ν_{max} (cm^{-1}): 3265 (-OH); 3060 (Arom.C-H); 2926 (Aliphatic C-H); 1677 (N=N); 1090 (C-O). ^{1}H-NMR (DMSO-d_6), δ(ppm): 5.85 (s, 2H, -CH); 4.75 (s, 4H, -CH_2); 2.54 (s, 6H, -CH_3); 6.60-7.85 (m, 20H, Arom.C-H); 10.42 (s, 2H, -OH), 9.80 (s, 2H, -OH).

Synthesis of 25,27-bis-[4-(3-methyl-1'-phenyl-5'-pyrazolon-4-yl-azo) benzyloxy]-26,28- dihyroxythiacalix[4]arene (4h)

Yield: 0,073 g, **47,7%; mp:** 220-230 ºC **FT-IR,** ν_{max} (cm^{-1}): 3268 (-OH); 3060 (Arom.C-H); 2922 (Aliphatic C-H); 1677, 1594 (N=N); 1090 (C-O). ^{1}H-NMR (DMSO-d_6), δ(ppm): 6.05 (s, 2H, -CH); 4.79 (s, 4H, -CH_2); 2.25 (s, 6H, -CH_3); 6.60-7.25 (m, 30H, Arom.C-H); 8.15 (s, 2H, -OH).



Scheme 5. General Reaction Scheme of Synthesized Compounds

Absorption Study:

In this part of our study, the effects of the substituents, different solvents and the pH of the medium on the colors of the azo dyes obtained were investigated. The change in maximum absorption wavelengths in these solvents was examined. The concentrations in each solvent are different due to the resolution. Protic solvents can form hydrogen bonds with the electron pair of the carbonyl group oxygen. In this case, while reducing the n energy level, π * energy level does not bring a change occurs.

Solvent Effect:

Visible absorption spectra of the synthesized azo dyes were obtained in six different solvents (DMSO, DMF, MeCN, MeOH, AcOH, $CHCl_3$).

Acid-Base Effect:

In this part of our study, the UV-visible region spectra of the dyes were taken by adding HCl and KOH in methanol to examine the absorption spectra of the compounds in acidic and basic environment.

3. Result

In the results of FT-IR spectrums, the broad bands resulting from O-H stretching vibrations were seen in the range of 3423-3264 cm^{-1}. The bands in the range of 3026-3064 cm^{-1} were assigned to aromatic C-H stretching vibrations, aliphatic C-H stretching vibrations were also identified at the range of 2962-2913 cm^{-1}. The peaks at the range of 1678-1594 cm^{-1} corresponded to N=N stretching and bending vibrations azo bridges. The peaks associated to C-O bonds were seen at 1090- 1001 cm^{-1}. The peaks at 3325 cm^{-1} were associated to -NH_2 stretching vibration only for compound 4. The peaks associated to NO_2 bonds were seen at 1512-1346 cm^{-1} only for compound 3 **(Table 1).**

Table 1: Values of FT-IR spectra of compounds.

Compound	FT-IR, υ_{max} (cm^{-1})						
	-OH	**-NH_2**	**Arom. C-H**	**Aliphatic C-H**	**N=N**	**NO_2**	**C-O**
1	3323		3026	2962			1087
2	3270		3062	2913			1063
3	3385		3060	2950		1512 1346	1001
4	3423	3325	3007	2919			1066
4a	3266		3060	2923	1678-1596		1090
4b	3264		3059	2926	1678-1596		1090
4c	3268		3064	2926	1678-1607		1090
4d	3267		3059	2926	1678-1607		1090
4e	3266		3059	2926	1678-1597		1090
4f	3265		3059	2922	1677		1090
4g	3265		3060	2926	1677		1090
4h	3268		3060	2922	1677-1594		1090

^{1}H-NMR spectral results for compounds 1, 2 and 3 were found to be consistent with the literature. And then the peak of OH proton for Compound 4 was observed at 11.25 ppm. While aromatic protons belonging to this structure were observed between 6,20 and 8,75 ppm, aliphatic protons were observed at 3,82 and 5,26 ppm. The amine protons in the compound were seen at 13.01 and 15.05 ppm (**Table 2)**.

When the NMR results obtained for the synthesized dyes were examined, the peaks of OH protons were seen between 8.12-11.65 ppm. Aromatic protons were obtained between 6.50-9.06 ppm and aliphatic protons were obtained between 2.25-6.18 ppm. The proton of the imine was observed at 9.57 ppm only for the compound 4f (**Table 2)**.

The integration rates obtained from the NMR results are proportional to the structures of the synthesized compounds.

Table 2: Values of ^{1}H-NMR spectra of compounds.

Compound	**^{1}H-NMR δ(ppm)**			
	Ar-OH	**Arom. C-H**	**Aliphatic C-H**	**$-NH_2$, -NH**
1	9,63 (s, -OH)	7,67 (s, 8H, Arom.C-H)	1,25 (s, 36H, tert-buthyl)	
2	9,45 (-OH)	8,50-8,42 (m, 12H, Arom.C-H)		
3	7,88 (s,2H,-OH)	6,81, 7,09, 7,79 (m, 12H, Arom.C-H); 7,61, 8,21 (d,d, 8H Arom.C-H)	5,51 (s, 4H, $-CH_2$)	
4	11,25 (s, 2H,-OH)	6,20, 8,75 (m, 20H, Arom.C-H)	3,82, 5,26 (s, 4H, $-CH_2$)	13,01, 15,05 (s, 4H, $-NH_2$)
4a	11.20, (s, 2H,-OH), 9.80 (s, 2H,-OH)	6.68-8.81 (m, 32H, Arom.C-H)	4.76-4.80 (s, 4H, $-CH_2$)	-
4b	11.65 (s, 2H,-OH), 9.90 (s, 2H,-OH)	7.05-8.94 (m, 28H, Arom.C-H)	4.91 (s, 4H, -CH2)	-
4c	11.05, 9.80 (s, 4H,-OH	7.14-8.84 (m, 30H, Arom.C-H)	4.90 (s, 4H, $-CH_2$)	-
4d	11.10, 12.85 (s, 4H,-OH	7.12-8.89 (m, 28H, Arom.C-H)	4.88 (s, 4H, $-CH_2$)	-
4e	11.10, 10.05 (s, 4H,-OH	7.05-9.06 (m, 24H, Arom.C-H)	6.18, (s, 2H, -CH), 4.91 (s, 4H, $-CH_2$)	-
4f	8.12 (s, 2H,-OH	6,50- 8,15 (m, 20H, Arom.C-H)	5.89 (s,1H,CH),4.79 (s, 2H, $-CH_2$), 2.25 (s,3H,CH_3)	9.57 (s,1H,NH)
4g	10.42,9.80 (s, 2H,OH)	6,60- 7,85 (m, 20H, Arom.C-H)	5.85 (s,1H,CH),4.75 (s, 2H, $-CH_2$), 2.54 (s,3H,CH_3)	-

4h	8.15 (s, 2H,OH)	6,60- 8,25 (m, 30H, Arom.C-H)	6.05 (s,1H,CH),4.79 (s, 2H, -CH_2), 2.25 (s,3H,CH_3)	-

When the absorption values of the compounds in different solvents are taken into consideration in the spectra taken in DMSO, the compound 4a shows a double maximum, while the other compounds show a single maximum. The spectra of compounds 4a, 4c are observed at long wavelengths. When the spectrum in DMF is examined, it is observed that the compound 4c gives a double maximum while the others have a single maximum. 4a is seen at long wavelength, and 4c at short wavelength. In the spectra in acetonitrile, the compound 4a gives a double maximum while the others have a single maximum. The 4a and 4c compounds are seen at long wavelength and the 4b compound at short wavelength. When the spectrum in methanol is examined, it is observed that all compounds give a single maximum. 4a and 4d compound at short wavelength. When the spectrum in acetic acid is examined, it is observed that the compound 4a gives a double maximum, while the compound 4e does not give a maximum and the other compounds have a single maximum. 4a, 4c compounds at long wavelength, and 4b, 4d, 4f and 4g compounds at short wavelength. When the spectrum in chloroform is examined, it is observed that the compound 4a gives a double maximum while the others have a single maximum. 4a, 4d and 4f compounds at long wavelength and 4b and 4c compounds at shorter wavelength. According to these results, it can be said that the compounds are not in a single tautomeric form and may exist in different tautomeric forms (**Table 3)**.

Table 3: Values of UV-vis. spectra of compounds.

Compound	DMSO	DMF	Acetonitrile	Methanol	Acetic acid	Chloroform
4a	409 478 518 s	412 478 s 518 s	397 469 510 s	411 477 s	385 490 516 s	397 481 514 s
4b	422	417	421 398 s	423 394 s	432 395 s	434 394 s
4c	411 461 s 491 s	459 490 433 s	401 455 s	446	392 457 s	434 392 s
4d	419	414	405	415 389 s	421 388 s	363 389 s 429 s
4e	405	404	392	389	371 s	370
4f	411	409	403	405	411 370 s	354 421 s
4g	410	409	401	403	409 389 s	385
4h	403	402	396	396	396	397

S: Shoulder

When the spectrum in methanol + HCl is examined, the 4a and 4d compounds give a double maximum, while the 4c and 4e compounds do not give a maximum and the others have a single maximum. 4a is observed at long wavelength and 4b at short wavelength. The compounds 4a, 4c, 4d, 4g and 4h show hipsochromic shift when compared to the spectra taken in methanol, while the 4b and 4f compounds do not change much. When the HCl of 4e compound in methanol was added, it changed to hypsochromic shift and turned into short wavelength shoulder. When the spectra in methanol + HCl are examined in general, it is observed that λmax values are hipsochromic shift according to the spectra taken in methanol. When the spectrum in methanol + KOH is examined, it is observed that all compounds have a single maximum. Shoulders of 4a, 4b, 4d and 4h are seen at long wavelength. Compared to the spectra taken in methanol, other compounds except for 4b and 4c were observed to have been subjected to a bichocromic shift. When the spectra in methanol + KOH are examined in general, it can be concluded that λmax values have been subjected to the batochromic shift according to the spectra taken in methanol (**Table 4**).

Table 4: Values of UV-vis. spectra of compounds in acidic and basic solvents.

Compound	Methanol	Methanol + KOH	Methanol + HCl
4a	411	431	376 482
	477 s	456 s	513 s
4b	423	388	426
	394 s	452 s	394 s
4c	446	436	417
4d	415	426	390 421
	389 s	495 s	
4e	389	437	
			378 s
4f	405	427	422
4g	403	437	357
4h	396	396	393
		428 s	

S: Shoulder

The colors from the left to right of the 4a, 4b, 4c, 4d, 4e, 4f, 4g, 4h azo dyes we synthesize are shown below (**Figure 1)**.

Figure 1. Color scale of synthesized compounds

The color states of the compound 4a at 25 ºC at different pH values are shown below. In the acidic environment, the shades of orange color shift to purple hues in the basic environment (**Table 5 and Figure 2)** .

Table 5. Colors of compound 4a at different pH values.

1	2	3	4	5	6	7	8	9	10	11	12
2,70	2,79	2,88	2,98	3,44	8,15	9,23	10,3	11,55	12,09	12,37	12,48

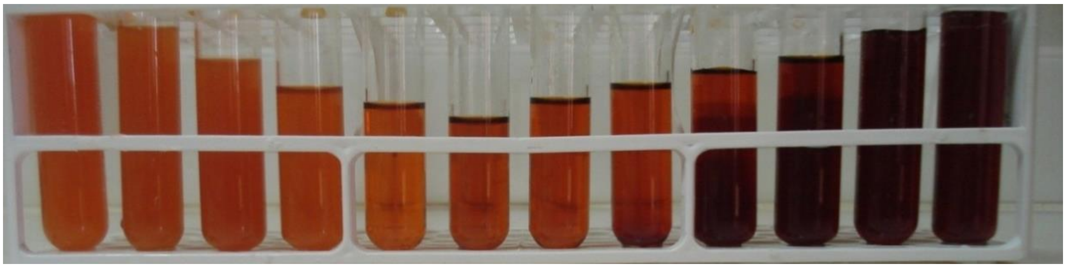
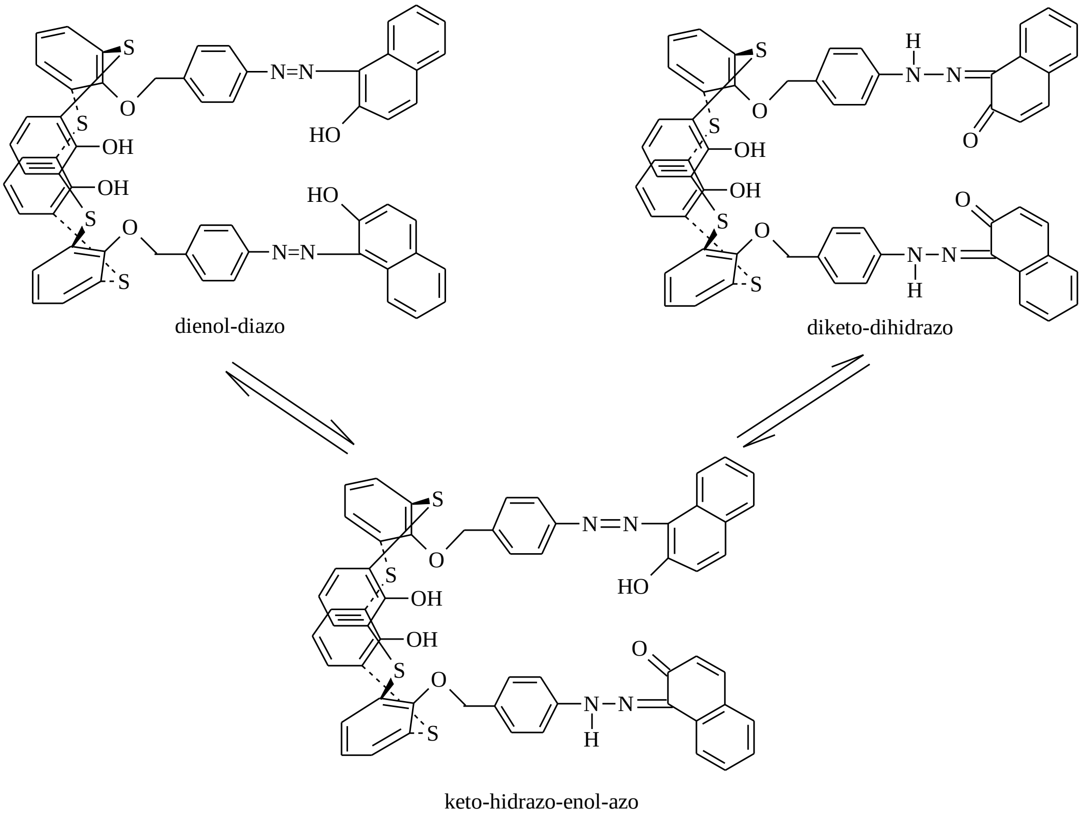


Figure 2. Solvents of compound 4a at different pH values

4. Discussion and Conclusion

Obtained from the analysis results; the synthesized dyes have different tautomeric structures. As shown in **Scheme 6**, several of the possible tautomeric forms on the compound 4a are shown. Of these, diketo-dihydrazo, dienol-diazo, keto-hydrazo-enol-azo are given. Apart from these, there are different representations of these tautomers and anionic and cationic tautomers.

In the structures containing the hydroxyl group in the FT-IR spectrum of the synthesized compounds, the peaks observed in the -OH group and the absence of any peaks of the carbonyl group indicate that the compound may be present in the solid dienol-diazo tautomeric form.



Scheme 6. Possible tautomeric structures of compound **4a**.

As a result, eight different dyes of thiacalix[4]arene were successfully synthesized and macrocyclic chemistry was introduced into new compounds.

5. References

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