

Research on Synthesis of New Azo Calix[4]arene and its Dyeing Properties

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ABSTRACT: With the raw materials of calix[4]arene, benzocaine, tricaine and procaine hydrochloride, three new azo calix[4]arene derivatives—6a, 6b and 6c are synthesized by diazotization-coupling reaction of an aromatic amine, with its yield of 83%, 81% and 83% respectively. The structural characterization is in a way of IR, ¹H NMR and elemental analysis. This paper investigates the spectral properties of azo calix[4]arene derivatives under different solution pH conditions through the UV-visible spectroscopy, and researches the dyeing properties through the dyeing curve, color yield test and fastness test. The results show that, with the increase of pH value, the azo calix[4]arene derivatives—6a, 6b and 6c form azo-hydrazone tautomeric isomers with the maximum absorption peak redshift; the dyeing effect of the compound is good, of which the dye-uptake rate of the compound 6a is as high as 78%; the surface depth of color yield is 2.798, and the dry and wet rubbing fastness and the soaping fastness are respectively 4, which is a better disperse dye.

Keywords: azo calix[4]arene; diazotization-coupling reaction; azo-hydrazone tautomeric isomers; dyeing

1 INTRODUCTION

Disperse dye is currently the largest species in the production of dyes, which is often used in dyeing for polyester fiber and acetate fiber. The development of new disperse dyes with excellent dyeing properties and expansion of its scope of application have important practical significance.

Calixarenes is the third generation of supermolecule after crown ether and cyclodextrin^[1], which is a cyclic oligomer connected with a phenol unit by methylene. It is characterized by adjustable cavity, convertible conformation, easy chemical modification and functionalization, easy synthesis, inexpensive raw materials and so on^[2]. In recent years, with in-depth study of host-guest chemistry, the functional modification and application of the calixarenes become a popular research topic in this field^[3]. The chromophoric group has become one of the research directions on the functional modification of the calixarenes. By using the diazotization-coupling of the aromatic amine^[4], the oxidation-coupling of phenol aromatic ring^[5] and other methods, the azo group can be introduced into the calixarene to constitute a host molecule with the color recognition function. Currently, the compound of azo group calixarene mainly contains nitrophenylazo calix[4]arene^[6], phenylazo calix[6]arene^[7], bis azo group bridged calix[8]arene^[8],

thiazolyalzo calix[n]arene^[9], methylisoxazole azo group calix[4]arene^[10] and thiadiazole azo group calix[4]arene^[11]. Such compound has the nature of the calixarene and azo compounds, which is a type of dye, indicator and heavy metal complexing agent with special selectivity. This paper directly makes the azo group calix[4]arene as a dye, and such article is rarely reported. It is not only of great significance to the development of new disperse dyes with excellent dyeing properties, but also opens up a new application field for the disperse dyes.

In this paper, we synthesize the tert-butyl calix[4]arene with the raw materials of the tert-butyl phenol and formaldehyde, and then synthesize the calix[4]arene with the raw materials of the tert-butyl calix[4]arene after the dealkylation reaction in the presence of the anhydrous aluminum chloride, and finally synthesize three new derivatives of azo group calix[4]arene through the diazotization-coupling action of the aromatic amines. The synthetic route is shown in Figure 1, and the structural characterization is in a way of IR, ¹H NMR and elemental analysis. This paper investigates the impact of the solution pH on the spectral properties of the synthetic compounds via UV-Vis, analyzes the changes of hydrazone form in the azo-hydrazone tautomeric isomers under different pH values, and researches dyeing process under acidic and alkaline conditions, and researches the

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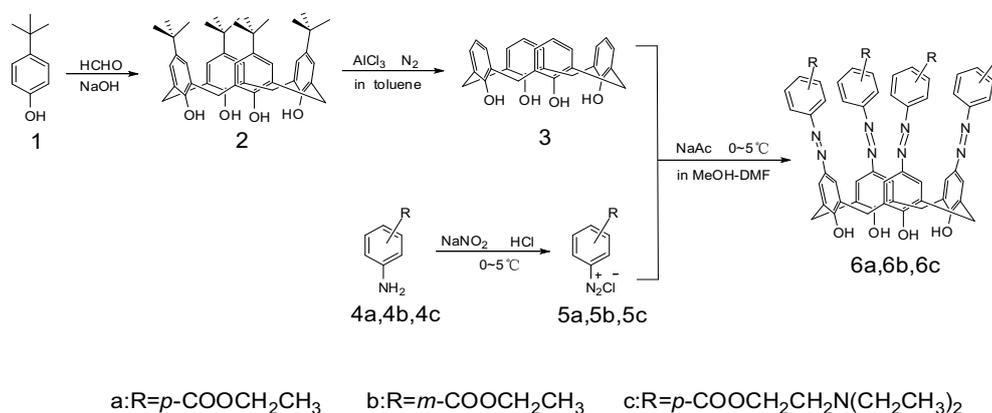


Figure 1. Synthetic route of the azo group calix[4]arene (6a - 6c)

dyeing properties through the dyeing curve, color yield test and fastness test.

2 MATERIALS AND METHODS

2.1 Material, instrument and agents

Material: polyester fabric

Instrument: INOVA 600NB hydrogen NMR; VarioIII elemental analyzer; VERTEX 70 Fourier transform infrared spectrometer; UV-visible absorption spectrometer ultraspec 3000 pro.

2.2 Experiment

2.2.1 Synthesis of tert-butyl calix[4]arene and calix[4]arene

Refer to the references [12, 13] to synthesize the tert-butyl calix[4]arene, and refer to the reference [14] to synthesize the calix[4]arene.

2.2.2 General method of synthesis of Compound 5

The method is to weigh 10mmol of aminobenzoate to be dissolved in 10ml of methanol-water (methanol: water=1: 1), and add 2ml of concentrated hydrochloric acid, and cool it to 0°C - 5°C, and then weigh 0.7g of sodium nitrite (10mmol) to be dissolved in 3ml of water (cool it to 0°C - 5°C), and dropwise add the sodium nitrite to the former solution through stirring and ice-bath. The entire process is controlled at 0°C - 5°C, the reaction time is 30min, so as to obtain 5a diazonium salt solution. The Congo red test paper can be used to test the acidity, and the potassium iodide test paper can be used to test the nitrite. There is also a need to properly adjust the acidity and add the sodium nitrite.

2.2.3 General method of synthesis of Compound 6

The method is to slowly add aforementioned synthesized diazonium salt to the cold solution (0°C-5°C),

of which containing 1.0g (2.36mmol) of the tetracarbonyl calixarene and 4.08g (30mmol) of sodium acetate trihydrat—36ml of methanol-DMF-water (5:8:5v/v/v), and then separate out the red precipitate. The ice-bath time is 2h, the still standing is 2h at room temperature, and then the way is suction filtration, washing with water and drying. Recrystallization is done in methanol chloroform.

(6a) 5, 11, 17, 24-4[(4-ethoxycarbonyl-phenyl) azo group]-25, 26, 27, 28- tetrahydroxy-calix[4]arene

The yield is 83%, and the melting point is more than 300°C. IR, ν/cm^{-1} : 3331(-OH), 1718(C=O), 1464 (N=N), 1387(Ar). ¹HNM (600Hz, DMSO-d₆, ppm) δ : 8.04-8.05 (d, *J*=6Hz, 8H, ArH), 7.82-7.84(d, *J*=12Hz, 16H, ArH), 4.31-4.35(d, 24, 8H, ArCH₂Ar), 3.41(m, 8H, OCH₂) 1.31-1.34(t, *J*=18Hz, 12H, CH₃). Through elemental analysis, the measured value of C₆₄H₅₆N₈O₁₂ is as follows: C is 68.13; H is 4.97; N is 9.96. The calculated value is as follows: C is 68.07; H is 5.00; N is 9.92.

(6b) 5, 11, 17, 24-4[(3-ethoxycarbonyl-phenyl) azo group]-25, 26, 27, 28-tetrahydroxy-calix[4]arene

The yield is 81%, and the melting point is more than 300°C. IR, ν/cm^{-1} : 3227(-OH), 1713(C=O), 1548 (N=N), 1464(Ar). ¹H NM (400Hz, DMSO-d₆, ppm) δ : 7.84(s, 8H, ArH), 7.61-8.26(m, 12H, ArH), 9.24(s, 4H, OH), 4.30-4.35(m, 8H, OCH₃), 1.29-1.33(t, *J*=16Hz, 12H, CH₃). Through elemental analysis, the measured value is as follows: C is 68.14; H is 4.87; N is 9.95. The calculated value of C₆₄H₅₆N₈O₁₂ (Mr, 1129.18) is: C is 68.07; H is 5.00; N is 9.92.

(6c) 5, 11, 17, 24-4[(4-(2-(diethylamino)) ethoxycarbonyl phenyl) azo group]-25, 26, 27, 28-synthesis of the tetrahydroxy calix[4]arene

The yield is 83%, and the melting point is more than 300°C. IR, ν/cm^{-1} : 3439(-OH), 1718(C=O), 1564(N=N), 1412 (Ar). ¹H NM (400Hz, DMSO-d₆, ppm) 7.81-8.07(m, 8H, ArH), 6.65-7.00(dd, 12H, ArH), 4.43-4.45(t, *J*=12 Hz, 8H, OCH₂), 3.60-3.63(t, *J*=12 Hz, 8H, CH₂CH₂N), 0.97-1.01(t, *J*=16 Hz, 12H, CH₃). Through elemental analysis, the measured value is as follows: C is 67.94; H is 6.59; N is 11.91.

The calculated value of $C_{80}H_{92}N_{12}O_{12}$ (Mr, 1413.66) is as follows: C is 67.97; H is 6.56; N is 11.89.

2.2.4 UV absorption spectrum experiment

Take a certain volume of standard solution of calix[4]arene derivatives to 25ml of the volumetric flask, add 5ml of the buffer solution with known pH value, and dilute the solvents (water, methanol) to the scale and shake up. Take a portion of solution from a 1cm pathlength cuvette and place it in the optical path. With the reference of corresponding solvents, 200 - 800nm of wavelength absorption condition can be measured respectively.

2.2.5 Dyeing

Take 0.1g of dye into the beaker, add 2ml of DMF and 0.1g of dispersants, and then add 100ml of water in the breaker to adjust the pH value, and mix up with the glass rod. Pour the evenly stirred dye liquor into the steel bowl and put the polyester base cloth into the steel bowl after moisten it, and then put it into the high-temperature and high-pressure dyeing machine for dyeing 30min under the temperature of 130°C. After dyeing, the fabric is cleaned with the reductive cleaning agent. After the washing, we do soap boiling in a thermostatic water batch shock pan (the soap flake is 3g/L; the soda is 3g/L; the temperature is 50°C; the time duration is 45min; the bath ratio is 1:50), washing and drying.

2.2.6 Dye-uptake rate curve

Dyeing is in accordance with the process conditions. When dyeing begins, the dye-uptake rate shall be measured every 5min until the end of dyeing. The dye-uptake rate curve is developed with the dye-uptake rate as the vertical axis, and the time as the horizontal axis:

$$\text{Dye-uptake rate} = \left(1 - \frac{E_i}{E_0}\right) \times 100\%$$

Where: E_i represents the residual light absorbance of dye liquor (dilution factor to be considered); E_0 represents the absorbance of dye liquor.

2.2.7 Color yield depth test

The value of the surface depth of color yield (K/S) can be measured by Datercolor 400 computer color testing and matching instrument. The test specimens are folded as four layers. The average value can be obtained by measuring four times.

2.2.8 Soaping fastness, wet/dry rubbing fastness test

Please refer to the Standard GB/T 3921-1997 *Test Method of Washing Color Fastness of Textiles*. The fabric size is 4cm × 10cm; the temperature is 60°C; the time is 30 minutes; the soap powder is 5g/L; Na_2CO_3 is 2g/L; the liquor ratio is 1:50. After soaping, ISO grey scale can be used to assess the discoloration of test specimens and staining of adjacent fabric.

Please refer to the Standard GB3920-1997 *Test*

Method of Color Fastness to Rubbing of Textiles. After testing the parameters, there is a need to remove the testing fiber from the rubbing cloth, and the grey scale is used to assess the staining series of the rubbing cloth.

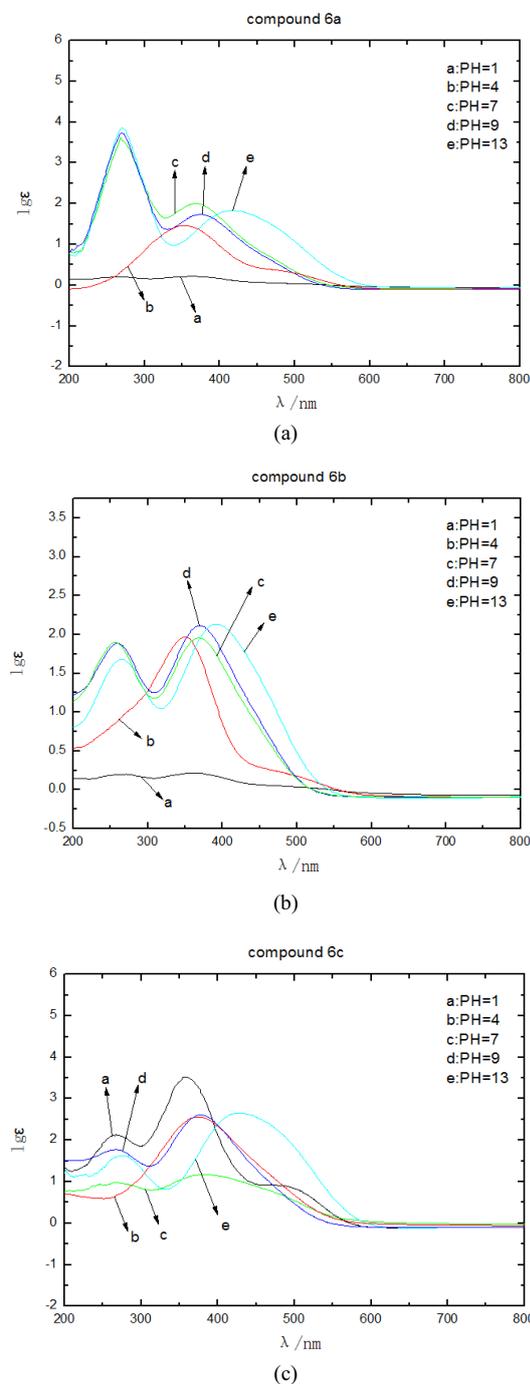


Figure 2. UV-visible absorption spectrogram of the compound 6 with the changes of pH value

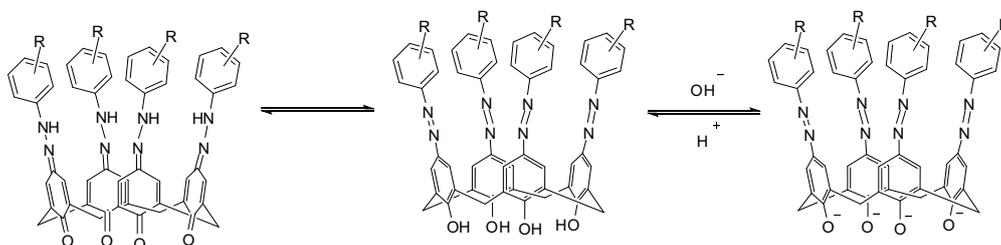


Figure 3. Balanced type of the azo-hydrazone tautomeric isomer of the compound 6a with the changes of pH value

Concentration is 5×10^{-5} mol/L, a: pH=1; b: pH=4; c: redshift.
pH=7; d: pH=9; e: pH=13

3 RESULTS AND DISCUSSION

3.1 Spectral properties

The synthesized azo group derivative of the calix[4]arene has multiple phenolic hydroxyl groups (-OH), multiple azo groups (-N=N-), 6c and multiple tertiary ammonia, so it may have ionization and proton changes under different pH values, resulting in the changes of visible ultraviolet absorption spectrum. Figure 2 is an ultraviolet absorption spectrogram under different pH values.

As can be seen from Figure 2, the absorption peak of the compounds 6a and 6b under the strong acid is almost zero; there is only one peak under the weak acid, and two peaks under the neutral, weak base and strong base; with the increase of pH value, there is the maximum absorption peak redshift. The absorption peak of the compound 6c under the neutral is almost zero; there is only one absorption peak under the weak acid, three absorption peaks under strong acid, and two absorption peaks under the weak base and strong base; with the increase of pH value, there is the maximum absorption peak redshift. The absorption peak of 0 is caused by complete precipitation of solid when pH value of the compounds 6a and 6b is less than 1, and pH value of the compound 6c is 7.

The azo group calixarene is a kind of calixarene derivative with the most potential to play a significant role in coloration. The azo-hydrazone tautomeric isomer is an important factor to cause coloration, while the acid-base effect has a significant impact on the azo-hydrazone tautomeric isomer [15, 16]. The azo-hydrazone tautomeric isomer of the azo calix[4]arene 6a has the following balance with the changes of pH value (Figure 3).

For the compound 6a, it is an azo group under neutral conditions and turns into hydrazone form under the weak acid. In the structure, $-C=N-$ occurs $n \rightarrow \pi^*$ transition [17]. Under alkaline conditions, the phenolic hydroxyl group in the molecules ionize, namely, $-OH$ turns into $-O^-$; it makes the oxygen atom increase lone pair electrons, thus greatly enhancing the electronic capability, making the compounds form a larger conjugated system, and leading to the absorption peak

3.2 Dyeing properties

3.2.1 Dyeing under acidic conditions

To dye with the high-temperature and high-pressure dyeing machine, pH value shall be controlled at 5 to 6. The acetic acid and ammonium dihydrogen phosphate are used to adjust the pH value. In order to maintain the dye bath to be stable, the dispersants and high-temperature leveling agents are added in dyeing. Dyeing is carried out in the acidic system, and the dyeing process shall measure the dye-uptake rate every five minutes, and the dye-uptake rate curve is developed. The results are shown in Figure 4:

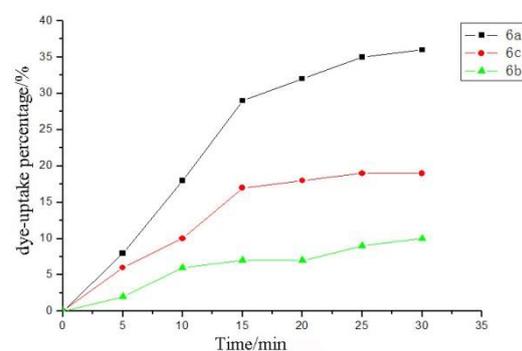


Figure 4. Dye-uptake curve of the compounds 6a, 6b and 6c

As can be seen from Figure 4, the dye-uptake rate of the dyeing system is very low, but the dye-uptake rate of the compound 6a is higher than that of other compounds.

3.2.2 Color yield test

To compare with the dyeing effect of the compounds 6a, 6b and 6c, the color yield parameters (L^* , a^* , b^* , c^* , K/S) are shown in Table 1.

In the test data, L, a, b, c values reflect the depth red and green, yellow and blue, and brilliant degree of the fabric color yield. As can be seen from Table 1, the color yield of 6a is 81.3, and the brilliant degree is 51.3 with the darkest color and maximum brilliant degree, indicating that the color is close to yellow, K/S

value is 2.798 with the maximum color yield, while the color yield of 6b and 6c is relatively low, so 6a is the most suitable as a disperse dye.

Table 1. Color yield test

Name	L*	a*	b*	c*	K/S
6a	81.3	5.33	51.03	51.3	2.798
6b	80.64	12.08	36.3	38.26	1.281
6c	69.7	13.53	28.67	31.7	1.87

3.2.3 Fastness test

The color fastness of the fabric means that the dyed fabric has the ability to maintain the original color state in the process of use or in subsequent processing when the dyes or pigments are affected by a variety of external factors. Its properties determine the application performance and application field of the fabric. Table 2 indicates that the test values of the dry and wet rubbing fastness and the soaping fastness of 6a, 6b and 6c.

Table 2. Fastness test

Name	6a	6b	6c
Dry rubbing fastness	4	2-3	3
Wet rubbing fastness	4	3	2-3
Soaping fastness	4	3-4	3

As can be seen from Table 2, the dry and wet rubbing fastness and soaping fastness of the dyed fabric 6a is 4 which is relatively high, but it is relatively low for 6b and 6c, indicating that 6a can be good for the dyed fabric and dense combination.

4 CONCLUSIONS

In this paper, we synthesize three kinds of new azo calix[4]arene dyes through a series of reaction, and adopt the infrared spectroscopy, nuclear magnetic resonance spectrum, elemental analysis and other means to characterize their structures. This paper also adopts the UV-visible spectrophotometry to research the absorption spectral features of these three kinds of derivatives of azo group calixarene under different pH values, and investigates the relationship between its structure and spectral features, and researches its dyeing properties. The results show that, with the increase of pH value, the azo calix[4]arene derivatives—6a, 6b and 6c form azo-hydrazone tautomeric isomers with the maximum absorption peak redshift; the dye-uptake rate of the compound 6a is as high as 78% with a better color yield test and fastness test, which is suitable as disperse dyes. This research not only has important theoretical significance on the disperse dyes with excellent dyeing properties, but also has practical application value for expanding the application scope of the disperse dyes.

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