Azocalix[4]resorcinarenes: their Antimicrobial Activity and Application in Dyeing of Fibers
Resume

The synthesized azocalix[4]resorcinarene dyes were screened for their antibacterial on *Staphylococcus aureus* (S. aureus), *Escherichia coli* (E. coli) and antifungal activity on *Rhizopus sp.* and *Asperillus niger* (A. niger). These azocalix[4]resorcinarene dyes have also been used for dyeing textile fibres like cotton, silk and wool. Their fastness properties towards light, water, washing and acid-alkali perspiration have also been studied and discussed. The position of color in CIELAB coordinates (L*, a*, b*, H* and C*) was assessed. These dyes exhibit good antimicrobial activity and fastness properties.
Chapter 6

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1. Introduction

Calixresorcinarenes is well represented in the literature due to the easiness of their synthesis\textsuperscript{[1]}, by the acid–catalyzed condensation of resorcinol with aliphatic or aromatic aldehydes. They are ideal frameworks and a readily available molecular platform\textsuperscript{[2]} for the development of chromogenic ionophores in the molecular recognition of ionic species of chemical and biological interest since the incorporation of a suitable sensory group in to the calixresorcinarene result in a chromogenic receptor. Though many research plans have been involved towards this end\textsuperscript{[3-7]}, and though there exists some research wherein macrocycles such as crown ethers\textsuperscript{[8]}, calix[4]pyrrole\textsuperscript{[9]} and calixarenes\textsuperscript{[10-13]} have been used as components for the preparation of azo dyes, the research in the area of azocalix[4]resorcinarene dyes\textsuperscript{[14]} has not evolved much.

Given their versatility of applications in various fields, azo compounds are one of the most widely used classes of dyes, accounting for more than half the dyes in commercial use. These dyes and pigments are therefore the most varied synthetic organic colorants in use today\textsuperscript{[15-18]}.

Azo compounds are a significant class of organic colorants and consist of at least a conjugated chromophore azo (-N=N-) group and two or more aromatic rings. The coloring properties of organic dyes depend on both the presence of the chromophore groups and the crystallographic arrangement of molecules in the solid state\textsuperscript{[19]}.

Dyes are substances that can be used to impart color to other materials, such as textiles, foodstuffs and papers. Unlike pigments, dyes are absorbed to a certain extent by the material to which they are applied. The dye is usually used as an aqueous solution and may require a mordant to improve the fastness of the dye on the fiber.

Dyes are classified according to how they are used in the dyeing process.
Acid dyes
These are water soluble anionic dyes that are applied to fibers such as silk, wool, nylon and modified acrylic fibers from neutral to acid dye baths. Attachment to the fiber is attributed, at least partly, to salt formation between anionic groups in the dyes and cationic groups in the fiber. Acid dyes are not substantive to cellulosic fibers.

Basic dyes
They are the water soluble cationic dyes that are applied to wool, silk, cotton and modified acrylic fibers. Usually acetic acid is added to the dye bath to take up the dye onto the fiber. Basic dyes are also used in the coloration of paper.

Direct (Substantive) dyes
Dyeing is normally carried out in a neutral or slightly alkaline dye bath, at or near the boil, with the addition of either sodium chloride (NaCl) or sodium sulphate (Na₂SO₄). Direct dyes are used on cotton, paper, leather, wool, silk and nylon. They are also used as pH indicators and as biological stains.

Mordant dyes
As the name suggests these dyes require a mordant. This improves the water, light and perspiration fastness of the dye on the fiber. Here the choice of mordant is very important as different mordant can change the final color significantly. Most natural dyes are mordant dyes and therefore there is a large literature base describing related dyeing techniques.

Vat dyes
These dyes are essentially insoluble in water and incapable of dyeing fibers directly. However, reduction in alkaline liquor produces the water soluble alkali metal salt of the dye. In this leuco form these dyes have an affinity for the textile fiber. Subsequent oxidation reforms the original insoluble dye.

Reactive dyes
Reactive dyes first appeared commercially in 1956 and were used to dye cellulosic fibers. The dyes contain a reactive group that, when applied to a fiber in a weak alkaline dye bath, form a chemical bond with the fiber. Reactive dyes
can also be used to dye wool and nylon, in the latter case they are applied under weak acidic conditions.

**Disperse dyes**

These were originally developed for the dyeing of cellulose acetate. They are substantially water insoluble. These dyes are finely ground in the presence of a dispersing agent then sold as a paste or spray dried and sold as a powder. They can also be used to dye nylon, triacetate, polyester and acrylic fibers. In some cases a dyeing temperature of 130°C is required and a pressurized dye bath is used. The very fine particle size gives a large surface area that aids dissolution to allow uptake by the fiber. The dyeing rate can be significantly influenced by the choice of the dispersing agent used during grinding.

**Azoic dyes**

Azo dyes involve the use of a dyeing technique in which an insoluble azo dye is produced directly onto or within the fiber. This is achieved by treating a fiber with a diazo component and a coupling component. With suitable adjustment of dye bath conditions the two components react to produce the required insoluble azo dye. This technique of dyeing is unique in that the final color is controlled by the choice of the diazo and coupling components.

**Food dyes**

One other class which describes the role of dyes, rather than their mode of use, is the food dye. Because food dyes are classed as food additives, they are manufactured to a higher standard than some industrial dyes. Food dyes can be direct, mordant and vat dyes and their use is strictly controlled by legislation. Many are azoic dyes, although anthraquinone and triphenylmethane compounds are used for colors such as green and blue. Some naturally-occurring dyes are also used.

**Sulphur dyes**

The first sulphur dye was discovered in France in 1873, and further work done by Raymond Videl enabled the manufacture of "Videl black". Its outstanding fastness to light, washing and boiling far surpassed any cotton black known at that time. Two disadvantages of sulphur dyes are that they produce dull shades
and lack a red. The main advantage lies in their cheapness, ease of application and good wash fastness. In their normal state sulphur dyes are insoluble in water but are readily soluble in the solution of sodium sulphide. In this form they have high affinity to the all cellulose fibers.

The investigation on antimicrobial activity of different types of compounds is not only useful for the development of new drugs but it is also essential to ascertain the toxic nature of the compound. Further, if a compound is to be used as a dye for fibers then it is always worthwhile to ascertain its biological properties in order to find its biocompatibility. In the present work the biological activity in terms of their growth inhibitory property on specific known bacterial and fungal cultures of the seven synthesized azocalix[4]resorcinarene dyes have been evaluated by the standard “disc diffusion” method. Bacterial subcultures of *E. coli* and *S. aureus* and fungal subculture of *A. niger, Rhizopus sp.* have been used as test organisms and all the samples have been tested against these stains at different concentrations. Further, it is the first report in which antimicrobial activity of azocalix[4]resorcinarene dyes has been reported. The dyeing performance of azocalix[4]resorcinarene dyes on fibers like cotton, wool and silk as well as their fastness properties related to light, water, washing and perspiration have also been studied and discussed.

2. Experimental

2.1. Materials and instrumentations

All the reagents used were of AR grade, purchased from Sigma-Aldrich or Fluka and were used without further purification. All aqueous solutions were prepared with deionised double distilled water, which was further purified by a Millipore Milli-Q water purification system (Millipack 20, Pack name: Simpak 1, Synergy). UV/Vis absorption studies were carried out on a JASCO 570 UV/Vis/NIR spectrophotometer using 10 mm quartz cells. Color coordinates (L*, a*, b*, H* and C*) were measured by Premier color scan 5100; computerized color matching system with illuminates D65 with 10° observer. Seven novel tetra functionalized azocalix[4]resorcinarene dyes (Figure 1) were synthesized and characterized as described in Chapter 2.
Figure 1. Azocalix[4]resorcinarene dyes

4a $R_1 = H, R_2 = Cl$
4b $R_1 = H, R_2 = NO_2$
4c $R_1 = H, R_2 = CH_3$
4d $R_1 = H, R_2 = OCH_3$
4e $R_1 = H, R_2 = COOH$
4f $R_1 = OH, R_2 = H$
4g $R_1 = H, R_2 = H$
2.2. Antimicrobial activities

a. The evaluation of antimicrobial activities involved the following general steps:

- Treatment of glass apparatus and its sterilization:
  All the glass apparatus, including petri-dishes were cleaned with chromic acid followed by washing with distilled water. These were then sterilized by heating at 120°C in an oven fully wrapped in inert foil for 6-8 hours.

- Preparation of the media and its sterilization:
  Nutrient agar and Czapek Dox agar slants were used as culture media for bacterial cells and fungal spores respectively.

Composition of nutrient agar medium is:
Peptone = 5.0 gm, sodium chloride = 5.0 gm, beef extract = 1.5 gm, yeast extract = 1.5 gm, agar = 15 gm, distilled water = 1000 ml (pH = 7.4±0.2)

Czapek Dox Agar medium was composed of:
sodium nitrate = 2.0 gm, dipotassium hydrogen phosphate = 1.0 gm, magnesium sulphate = 0.5 gm, potassium chloride = 0.5 gm, ferrous sulphate = 0.01 gm, sucrose = 30.0 gm, agar = 15.0 gm, distilled water = 1000 ml (pH = 7.3±0.2)

For preparation of the media, all ingredients except agar were dissolved in half of the water with gentle warming wherever required. In the remaining half of the distilled water, agar was dissolved by heating with constant stirring. The two solutions were mixed and heated to make a homogenous solution. One liter solution of each media was filtered through cotton and a clear solution was obtained. This was then sterilized, properly plugged in a conical flask by autoclaving at 120°C for 30 minutes.

- pouring of the media into sterilized petri-dishes and its solidification:
  15-20 ml of sterilized media was poured homogenously into sterilized petridishes and used for the inoculation.

- Inoculation of the media with the test organisms:
  Bacterial cells (0.5 ml) or of fungal spore suspension (0.2-0.3 ml) was added to the petridishes, prepared by the method as described above and spread with...
the help of a sterile spreader. These petridishes were kept in laminar for 10 minutes for inoculation.

- **Preparation of the solutions and control:**

  Standard solutions of compounds were prepared, 50 and 100 ppm solutions were prepared by appropriate dilution of stock solution and used to study their antimicrobial activity.

- **Preparation of test plates:**

  Filter paper discs were soaked in the above solution of test compound and these paper discs were placed on the petridish and incubated at 37°C for 24 hours.

- **Measurement of the zone of inhibition:**

  Zone of inhibition was measured for each compound separately with respect to control and also compared with standard drugs.

**b. General method used for the determination of antimicrobial activity:**

A saturated solution of nutrient agar or Czapek Dox agar (75.0 gm) was prepared in double distilled water and it was autoclaved for 15 minutes, then poured into petridishes in the laminar. After its solidification loan of bacteria (i.e. *E. coli* and *S. aureus*) or fungi (i.e. *A. niger* and *Rhizopus sp.*) against which antimicrobial activity is to be investigated was applied. Separate paper discs were soaked in both 50 and 100 ppm solution of all the azocalix[4]resorcinarene dyes for 10 minutes. These paper discs were then placed in petri-dishes and were kept in incubator at 37°C for 24 hours they were then removed and the zone of inhibition was measured in mm.

**2.3. Scouring of fibers (Cotton, Silk and Wool)**

2.0 gm caustic soda (NaOH) and 2.0 gm common detergent were mixed in 200 ml water and then 3.5 gm fiber hunk was added to this. The mixture was boiled for 3 hours and then allowed to cool at room temperature; the hunk was washed thoroughly with water to completely remove the adhered caustic soda and detergent.
2.4. Dyeing of fibers (Cotton, Silk and Wool)

In a dyeing bath, 0.5% of azo calix[4]resorcinarene dye was dissolved in a neutral or slightly alkaline solution. To this, 5 ml of 30% aqueous, (NaCl) or (Na₂SO₄), solution was added. The scoured fiber hunk (3.5 gm) was then added to the dyeing bath and its temperature was maintained at (~90°C) for 30 minutes. The dyed hunk was then removed, rinsed with cold water and dried.

2.5. Color measurements of dyed fibers

The color matching of the dyed fabrics against the standard has been studied by computerized premier color scan 5100. Their L*, a*, b* values as well as the color difference values such as △L*, △a*, △b*, △C*, and △H have been reported.

2.6. Studies for fastness properties [20]

It is a fundamental requirement that colored fibers should withstand conditions like exposure to light, washing, perspiration, etc., during their subsequent use. These conditions usually result in alteration in depth, hue, or brightness of the fibers. Some of the parameters that have been studied are as follow:

2.6.1. Fastness to water (As per IS: 767-1988)

A pair of dyed and undyed specimen was immersed in water for 30 minutes. Thereafter the water was drained and the hunks were dried separately and the change in color of the dyed hunks and the staining of the undyed hunks were assessed by means of the standard grey scale, where a rating of 5 is considered as excellent and 1 is poor.

2.6.2. Fastness to washing (As per IS: 764 –1979) (Test-3))

A pair of dyed and undyed specimen was immersed in 0.5% common detergent solution and agitated for 30 minutes at 60°C. The specimens were removed, rinsed three times with water and then dried. Change in color was assessed using the standard grey scale, where a rating of 5 is considered as excellent and 1 is poor.
2.6.3. Fastness to perspiration (As per IS: 971-1983)

Both acidic and alkaline solutions were used in this test. The tests were carried out in dry atmosphere at 38-40°C in a glass test tube. The change in color of the dyed and staining of the undyed specimen were assessed.

2.6.4. Fastness to light (As per IS: 686 –1985)

Half the dyed specimen was exposed to daylight for 10 hours and half of it was kept unexposed. The specimen was then evaluated for color loss. The reference standard chosen for light fastness is a series of eight blue dyes on wool where a rating of 8 is considered as excellent and 1 is poor.

3. Results and discussion

3.1. Antibacterial and antifungal activity of synthesized dyes

3.1.1. Antibacterial activity

The antibacterial activity of the compounds against *E.coli* and *S.aureus* were carried out using Muller Hinton Agar media (Hi media). The activity, reported in (Table 1), was carried out using paper disc method. Base plates were prepared by pouring 10 ml of autoclaved Muller-Hinton agar into sterilized Petri-dishes and allowing it to settle. Molten autoclaved Muller Hinton that had been kept at 48°C was incubated with a broth culture of the *E.coli* or *S.aureus* and then poured over the base plate. The discs were air dried and placed on the top of agar layer. The solutions of all compounds were prepared at two different concentrations and chloramphenicol was used as a reference. The plates were then incubated for 18 hours at room temperature. Among the various compounds, p-(4-carboxyphenylazo) calix[4]resorcinarene, Dye (4e), has been found to be most effective against these microbes showing maximum clarity of zones, its antibacterial activity was found maximum against *E.coli*.

3.1.2. Antifungal activity

The antifungal activity of these compounds was checked by the agar plate technique for the *Rhizopus sp.* and *A. niger* fungi. The compounds were directly mixed to the medium in different concentrations. The fungus was placed on the medium and incubated at 28°C for 3-5 days. The growth of fungus was
measured by recording the diameter of fungal colony. The following relation calculated the fungal growth inhibition:

Fungal growth inhibition (%) = A - \( B/A \times 100 \)

where A is the diameter of the fungal colony in the control plate and B is the diameter of the fungal colony in the test plate. Results are represented in (Table 2). Among all compounds p-(4-chlorophenylazo) calix[4]resorcinarene, Dye (4a), had shown maximum antifungal activity. Further it is interesting that the same compound has shown minimum zone of inhibition when screened for antibacterial activity against *E.coli* and *S.aureus*.

3.2. Color measurements

Color is associated with several aspects that create feelings and sensations or stimulus in the observer's mind. If the primaries chosen are red, green, and blue, a very large numbers of colors can be matched. Based on this theory, in 1931 the CIE [Commission Internationale de l'Eclairage (CIE)] [2-] developed a system for specifying color. In 1976 the CIE specified a new color space known as CIE 1976 (L* a* b*) color space or CIELAB. CIELAB allows the specification of color stimuli in terms of a three-dimensional space. The L* axis is known as the lightness and extends from 0 (black) to 100 (white). The other two coordinates a* and b* represent redness-greenness and yellowness-blueness respectively. If ΔL* is positive/negative the sample is lighter/darker than the standard. If ΔC* (chroma) is positive/negative the sample is stronger/weaker than the standard. ΔH indicates difference in hue.

In the present investigation, the applications of azo dyes derived from calix[4]resorcinarene are described for dyeing of cotton, silk and wool fibers. The samples were evaluated with the Premier color scan 5100, computerized color matching system with illuminants D_65 with 10° observer. The results of the color coordinates of the samples are given in (Table 3-5). They shows that ΔL values are negative for the dye (4a), (4d) and (4f) on cotton fiber, dye (4a), (4c) and (4d) on silk fiber and dye (4a) and (4c) on wool fiber which suggests that these samples are darker than the standard taken. The chroma values (ΔC) was negative for dye (4a), (4b), (4d), (4e) and (4f) on cotton fiber, dye (4a), (4c) and
(4d) on silk fiber and dye (4a), (4e) and (4f) on wool fiber, indicating their duller effect.

3.3. Dyeing and fastness properties

The structural and physical properties of the calix[4]resorcinarene, dyes (4a-4g), reveal that they may be classified as "direct dyes" for the dyeing of cotton, silk and wool. (Figure 2) shows that with the increase in dye concentration from 0.2 to 0.45, there is an increase in reflectance, after which there is negligible effect on reflectance with increase in the concentration of dye. It suggests greater availability of the dyestuff onto the fiber even at low concentrations.

The effect of varying the concentration of salt from 1.0 to 5.0 % on dyed fibers was assessed. The result showed that 3.0 to 5.0 % of aqueous salt did not have much effect on the reflectance of the fibers (Figure 3). When the fibers were dyed at various pH between 3.0-10.5 and its effect was studied by the reflectance measurements, it was observed that at a lower pH the dyeing was incomplete however the dyeing capacity was maximum between pH 6.5 and 8.0 but beyond pH 8, the dyeing capacity decreased gradually (Figure 4). (Figures 5, 6 and 7) show photographic representation of synthesized dyes (4a-4g) applied on cotton, silk and wool fibers.

The fastness properties of dyed fibers to washing, water, perspiration and light are summarized in (Table 6). The results show that fastness level is in between 3 and 5 indicating very slight alteration in the shade or loss in depth of the dye. Light fastness results were found to be 5-6, which indicates slight color loss of dyed fibers.
Conclusion

These dyes showed reasonable antimicrobial activity against selected microbes namely, E. coli, S. aureus and A. niger, Rhizopus sp. These azo calix[4]resorcinarenes being direct dyes can be considered as a good candidate for dyeing cotton, silk and wool fibers because of easy dyeing process, no after-treatment process required and possessing good fastness properties. Further, the dyed fabric showed good light fastness and good to excellent fastness to water, washing, staining and acid-alkali perspiration.
Table 1. Antibacterial activity of synthesized dyes

<table>
<thead>
<tr>
<th>Dye No.</th>
<th>Compound</th>
<th>Diameter of zone of inhibition in mm for E.coli</th>
<th>Diameter of zone of inhibition in mm for S.aureus</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>50 ppm</td>
<td>100 ppm</td>
</tr>
<tr>
<td>4a</td>
<td>p-(4-chlorophenylazo) calix[4]resorcinarene</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4b</td>
<td>p-(4-nitrophenylazo) calix[4]resorcinarene</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>4c</td>
<td>p-(4-methylphenylazo) calix[4]resorcinarene</td>
<td>7</td>
<td>11</td>
</tr>
<tr>
<td>4d</td>
<td>p-(4-methoxyphenylazo) calix[4]resorcinarene</td>
<td>6</td>
<td>9</td>
</tr>
<tr>
<td>4e</td>
<td>p-(4-carboxyphenylazo) calix[4]resorcinarene</td>
<td>7</td>
<td>12</td>
</tr>
<tr>
<td>4f</td>
<td>p-(2-hydroxyphenylazo) calix[4]resorcinarene</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>4g</td>
<td>p-(phenylazo)calix[4]resorcinarene</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Chloramphenicol*</td>
<td></td>
<td>11</td>
<td>22</td>
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</tbody>
</table>

* Chloramphenicol (An Antibiotic) has been taken as reference.
Table 2. Antifungal activity of synthesized compounds

<table>
<thead>
<tr>
<th>Dye No.</th>
<th>Compound</th>
<th>Fungal growth inhibition (%) with <em>Rhizopus</em> sp.</th>
<th>Fungal growth inhibition (%) with <em>A.niger</em></th>
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<tbody>
<tr>
<td>4a</td>
<td>p-(4-chlorophenylazo) calix[4]resorcinarene</td>
<td>65</td>
<td>54</td>
</tr>
<tr>
<td>4b</td>
<td>p-(4-nitrophenylazo) calix[4]resorcinarene</td>
<td>60</td>
<td>65</td>
</tr>
<tr>
<td>4c</td>
<td>p-(4-methylphenylazo) calix[4]resorcinarene</td>
<td>50</td>
<td>45</td>
</tr>
<tr>
<td>4d</td>
<td>p-(4-methoxyphenylazo) calix[4]resorcinarene</td>
<td>35</td>
<td>20</td>
</tr>
<tr>
<td>4e</td>
<td>p-(4-carboxyphenylazo) calix[4]resorcinarene</td>
<td>44</td>
<td>25</td>
</tr>
<tr>
<td>4g</td>
<td>p-(phenylazo)calix[4]resorcinarene</td>
<td>20</td>
<td>25</td>
</tr>
</tbody>
</table>
Table 3. Color coordinate values for calix[4]resorcinarene dyes on cotton fiber

<table>
<thead>
<tr>
<th>Dye No.</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>H</th>
<th>ΔL</th>
<th>Δa</th>
<th>Δb</th>
<th>ΔC</th>
<th>ΔH</th>
<th>ΔE</th>
<th>Str. %</th>
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<tbody>
<tr>
<td>4a</td>
<td>78.886</td>
<td>19.848</td>
<td>16.350</td>
<td>25.715</td>
<td>39.464</td>
<td>-0.010</td>
<td>-0.070</td>
<td>-0.029</td>
<td>-0.072</td>
<td>0.022</td>
<td>0.076</td>
<td>100.651</td>
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<tr>
<td>4b</td>
<td>75.618</td>
<td>18.306</td>
<td>16.190</td>
<td>24.438</td>
<td>41.473</td>
<td>0.001</td>
<td>-0.036</td>
<td>0.037</td>
<td>-0.003</td>
<td>0.052</td>
<td>0.052</td>
<td>99.837</td>
</tr>
<tr>
<td></td>
<td>(75.617)</td>
<td>(18.342)</td>
<td>(16.153)</td>
<td>(24.441)</td>
<td>(41.352)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4c</td>
<td>61.072</td>
<td>28.318</td>
<td>4.573</td>
<td>28.685</td>
<td>9.170</td>
<td>0.039</td>
<td>0.467</td>
<td>-0.015</td>
<td>0.458</td>
<td>-0.090</td>
<td>0.469</td>
<td>101.108</td>
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<tr>
<td></td>
<td>(61.033)</td>
<td>(27.851)</td>
<td>(4.588)</td>
<td>(28.226)</td>
<td>(9.351)</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4d</td>
<td>76.578</td>
<td>20.916</td>
<td>19.385</td>
<td>28.518</td>
<td>42.807</td>
<td>-0.012</td>
<td>-0.361</td>
<td>0.060</td>
<td>-0.225</td>
<td>0.288</td>
<td>0.366</td>
<td>99.256</td>
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<tr>
<td></td>
<td>(76.590)</td>
<td>(21.277)</td>
<td>(19.325)</td>
<td>(28.743)</td>
<td>(42.231)</td>
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<tr>
<td>4e</td>
<td>60.057</td>
<td>10.137</td>
<td>19.909</td>
<td>22.341</td>
<td>62.991</td>
<td>0.046</td>
<td>-0.210</td>
<td>-0.088</td>
<td>-0.018</td>
<td>0.227</td>
<td>0.232</td>
<td>99.850</td>
</tr>
<tr>
<td>4f</td>
<td>67.776</td>
<td>8.793</td>
<td>29.655</td>
<td>30.916</td>
<td>73.551</td>
<td>-0.018</td>
<td>0.028</td>
<td>-0.074</td>
<td>-0.063</td>
<td>-0.048</td>
<td>0.081</td>
<td>99.86</td>
</tr>
<tr>
<td></td>
<td>(67.794)</td>
<td>(8.711)</td>
<td>(29.729)</td>
<td>(30.979)</td>
<td>(73.639)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>4g</td>
<td>57.593</td>
<td>31.317</td>
<td>6.570</td>
<td>31.999</td>
<td>11.843</td>
<td>0.013</td>
<td>0.010</td>
<td>0.037</td>
<td>0.017</td>
<td>0.034</td>
<td>0.040</td>
<td>99.763</td>
</tr>
</tbody>
</table>

* Standard, if a* (positive) redness - (negative) greenness, b* (positive) yellowness - (negative) blueness and c* (positive) stronger – (negative) weaker
<table>
<thead>
<tr>
<th>Dye No.</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>H</th>
<th>ΔL</th>
<th>Δa</th>
<th>Δb</th>
<th>ΔC</th>
<th>ΔH</th>
<th>ΔE</th>
<th>Str. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>58.539 (58.602)</td>
<td>35.021 (35.145)</td>
<td>29.637 (29.737)</td>
<td>45.878 (46.038)</td>
<td>40.224 (40.219)</td>
<td>-0.063</td>
<td>-0.124</td>
<td>-0.100</td>
<td>-0.159</td>
<td>0.004</td>
<td>0.171</td>
<td>100.701</td>
</tr>
<tr>
<td>4b</td>
<td>64.536 (64.469)</td>
<td>29.500 (29.371)</td>
<td>24.959 (24.804)</td>
<td>38.642 (38.443)</td>
<td>40.217 (40.165)</td>
<td>0.067</td>
<td>0.129</td>
<td>0.155</td>
<td>0.199</td>
<td>0.035</td>
<td>0.212</td>
<td>101.064</td>
</tr>
<tr>
<td>4c</td>
<td>62.784 (62.796)</td>
<td>33.924 (33.965)</td>
<td>14.363 (14.382)</td>
<td>36.839 (36.884)</td>
<td>22.938 (22.940)</td>
<td>-0.012</td>
<td>-0.041</td>
<td>-0.019</td>
<td>-0.045</td>
<td>-0.002</td>
<td>0.047</td>
<td>98.779</td>
</tr>
<tr>
<td>4d</td>
<td>64.713 (64.760)</td>
<td>28.666 (28.807)</td>
<td>14.690 (14.801)</td>
<td>32.211 (32.387)</td>
<td>27.122 (27.183)</td>
<td>-0.047</td>
<td>-0.141</td>
<td>-0.111</td>
<td>-0.176</td>
<td>-0.034</td>
<td>0.186</td>
<td>98.607</td>
</tr>
<tr>
<td>4e</td>
<td>63.108 (63.078)</td>
<td>29.343 (29.232)</td>
<td>26.982 (26.912)</td>
<td>39.863 (39.734)</td>
<td>42.583 (42.617)</td>
<td>0.030</td>
<td>0.111</td>
<td>0.070</td>
<td>0.129</td>
<td>-0.024</td>
<td>0.135</td>
<td>100.582</td>
</tr>
<tr>
<td>4f</td>
<td>67.255 (67.192)</td>
<td>27.515 (27.516)</td>
<td>23.908 (23.724)</td>
<td>36.451 (36.331)</td>
<td>40.971 (40.751)</td>
<td>0.063</td>
<td>-0.001</td>
<td>0.184</td>
<td>0.120</td>
<td>0.140</td>
<td>0.194</td>
<td>101.098</td>
</tr>
<tr>
<td>4g</td>
<td>58.404 (58.345)</td>
<td>36.260 (36.170)</td>
<td>19.903 (19.756)</td>
<td>41.363 (41.214)</td>
<td>28.751 (28.632)</td>
<td>0.059</td>
<td>0.090</td>
<td>0.147</td>
<td>0.150</td>
<td>0.086</td>
<td>0.182</td>
<td>100.854</td>
</tr>
</tbody>
</table>

(*) Standard, if a* (positive) redness - (negative) greenness, b* (positive) yellowness - (negative) blueness and c* (positive) stronger - (negative) weaker
Table 5. Color coordinate values for calix[4]resorcinarene dyes on wool fiber

<table>
<thead>
<tr>
<th>Dye No.</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>H</th>
<th>ΔL</th>
<th>Δa</th>
<th>Δb</th>
<th>ΔC</th>
<th>ΔH</th>
<th>ΔE</th>
<th>Str. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>63.416 (63.444)</td>
<td>30.749 (30.984)</td>
<td>34.274 (34.305)</td>
<td>46.046 (46.226)</td>
<td>48.084 (47.893)</td>
<td>-0.028</td>
<td>-0.235</td>
<td>-0.031</td>
<td>-0.180</td>
<td>0.154</td>
<td>0.239</td>
<td>99.296</td>
</tr>
<tr>
<td>4b</td>
<td>63.551 (63.444)</td>
<td>30.633 (30.150)</td>
<td>33.408 (33.265)</td>
<td>45.326 (44.895)</td>
<td>47.462 (47.793)</td>
<td>0.107</td>
<td>0.483</td>
<td>0.143</td>
<td>0.431</td>
<td>-0.261</td>
<td>0.515</td>
<td>99.684</td>
</tr>
<tr>
<td>4c</td>
<td>51.077 (51.127)</td>
<td>36.160 (36.058)</td>
<td>15.162 (15.374)</td>
<td>39.210 (39.199)</td>
<td>22.739 (23.083)</td>
<td>-0.050</td>
<td>0.102</td>
<td>-0.212</td>
<td>0.011</td>
<td>-0.235</td>
<td>0.241</td>
<td>97.145</td>
</tr>
<tr>
<td>4d</td>
<td>64.974 (64.888)</td>
<td>31.601 (31.229)</td>
<td>40.496 (40.376)</td>
<td>51.367 (51.044)</td>
<td>52.012 (52.259)</td>
<td>0.086</td>
<td>0.372</td>
<td>0.120</td>
<td>0.323</td>
<td>-0.220</td>
<td>0.400</td>
<td>100.592</td>
</tr>
<tr>
<td>4e</td>
<td>60.283 (60.011)</td>
<td>10.096 (10.347)</td>
<td>19.871 (19.820)</td>
<td>22.289 (22.359)</td>
<td>63.041 (62.409)</td>
<td>0.272</td>
<td>-0.251</td>
<td>0.050</td>
<td>-0.070</td>
<td>0.246</td>
<td>0.373</td>
<td>101.501</td>
</tr>
<tr>
<td>4f</td>
<td>68.092 (67.794)</td>
<td>8.645 (8.711)</td>
<td>29.523 (29.729)</td>
<td>30.763 (30.979)</td>
<td>73.649 (73.639)</td>
<td>0.298</td>
<td>-0.066</td>
<td>-0.206</td>
<td>-0.216</td>
<td>0.005</td>
<td>0.368</td>
<td>102.500</td>
</tr>
<tr>
<td>4g</td>
<td>49.960 (49.886)</td>
<td>33.883 (33.742)</td>
<td>16.177 (15.995)</td>
<td>37.547 (37.341)</td>
<td>25.511 (25.353)</td>
<td>0.074</td>
<td>0.141</td>
<td>0.182</td>
<td>0.206</td>
<td>0.104</td>
<td>0.242</td>
<td>95.974</td>
</tr>
</tbody>
</table>

( ) Standard, if a* (positive) redness - (negative) greenness, b* (positive) yellowness - (negative) blueness and c* (positive) stronger – (negative) weaker
Table 6. Fastness properties of dyes on cotton, silk and wool fibers

<table>
<thead>
<tr>
<th>Dye</th>
<th>Water</th>
<th>Washing</th>
<th>Acid-Perspiration</th>
<th>Alkaline-Perspiration</th>
<th>Light - fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a b c d</td>
<td>a b c d</td>
<td>a b c d</td>
<td>a b c d</td>
<td>Cotton</td>
</tr>
<tr>
<td>4a</td>
<td>4 4 4 4</td>
<td>4 4 3-4 4</td>
<td>4 4 4 4</td>
<td>4 4 4 4</td>
<td>3-4</td>
</tr>
<tr>
<td>4b</td>
<td>4 4 4 4</td>
<td>4 3-4 4 4</td>
<td>4 4 4 5-4</td>
<td>4 4 4 4</td>
<td>4</td>
</tr>
<tr>
<td>4c</td>
<td>4 4-5 4 4</td>
<td>4 4 4 4</td>
<td>4 4-5 4 4-5</td>
<td>4 4-5 4-5 4-5</td>
<td>4</td>
</tr>
<tr>
<td>4d</td>
<td>4 4 4 4-5</td>
<td>4 4 4-5 4-5</td>
<td>4 4-5 4 4</td>
<td>4 4-5 4 4-5</td>
<td>3-4</td>
</tr>
<tr>
<td>4e</td>
<td>4 4 4 4-5</td>
<td>4 4 4 4-5</td>
<td>4 4-5 4 4</td>
<td>4 4-5 4 4-5</td>
<td>5-6</td>
</tr>
<tr>
<td>4f</td>
<td>4 4-5 4 4-5</td>
<td>4 4 4-5 4-5</td>
<td>4 4-5 4 4-5</td>
<td>4 4-5 4 4-5</td>
<td>5-6</td>
</tr>
<tr>
<td>4g</td>
<td>4 4 4-5 4</td>
<td>4 4 3-4 4</td>
<td>4 4 4 4</td>
<td>4 4-5 4 4-5</td>
<td>4</td>
</tr>
</tbody>
</table>

a: Alteration in shade of dyed fabric; b: Degree of staining of undyed cotton; c: Degree of staining of undyed silk; d: Degree of staining of undyed wool.
Figure 2. Effect of concentration of dyes on fibers
Figure 3. Effect of salt concentration on dyed fibers
Figure 4. Effect of pH on dyeing
Figure 5. Photographic representation of synthesized dyes (4a-4g) applied on cotton fiber
Figure 6. Photographic representation of synthesized dyes (4a-4g) applied on silk fiber.
Figure 7. Photographic representation of synthesized dyes (4a-4g) applied on wool fiber.
References


