A New Approach Towards Synthesis of Some Novel "Upper Rim" Functionalized Calix[4]resorcinarene Schiff-bases

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Abstract

Synthesis of new "upper rim" functionalized calix[4]resorcinarene Schiff-bases has been carried out by reacting tetra-aminocalix[4]resorcinarene with different aromatic aldehydes in ethanol at reflux temperature. The tetra-aminocalix[4]resorcinarene, which can serve as very good precursor for various derivatizations at the extra annular position, was synthesized for the first time through tetra-azo intermediate, by first introducing the azo functionality at the upper rim, and subsequent reduction with $Na_2S_2O_4$ in aq. NaOH. Synthesized Schiff-bases were characterized by elemental analysis, FT-IR, NMR and Mass spectral data. Their complexation ability with Cu(II) is also investigated.

Keywords: Calix[4]resorcinarene; upper rim; $Na_2S_2O_4$; Schiff-base

1. Introduction

Calixarene and its derivatives serve as excellent scaffolds (molecular platforms) for construction of sophisticated assemblies with versatile receptor properties.[1] Calixresorcinarenes are calixarene analogs,[2] possessing eight hydroxyl groups at extra annular position of the macrocycle. Calix[4]resorcinarenes deliver a versatile molecular platform for the elaboration of more complicated host system by virtue of its conformational flexibility. Their chemistry is focused mainly in two directions: (i) synthesis and application of host-guest complexes by non-covalent interactions and (ii) construction of novel supramolecular assemblies like dendrimers, nano-particles, nano-capsules and metal extractants.[3–6] Calix[4]resorcinarenes possess a relatively shallow conical cavity that can be extended by suitable substitution and further functionalization. Interest in calix[4]resorcinarene **1** has grown rapidly also because of the numerous derivatizations that can be realized, through relatively simple synthetic procedures, at their upper rim, methylene bridges and extra annular –OH groups.

Schiff-base, on the other hand, are versatile ligands and excellent reagents for biological and industrial purposes.[7–9] Schiff-bases have been widely studied for their co-ordination ability towards transition metals.[10–14] Thus, integration of the Schiff-base functionality on a calix[4]resorcinarene platform can give rise to interesting systems with some special recognition properties. With this in view, we report herein the first examples of calix[4]resorcinarene Schiff base derivatives.

In the present work, the tetra-aminocalix[4]resorcinarene was synthesized by an alternative procedure via aza intermediate. That is, Firstly the azo functionality was introduced at the upper rim of the calix[4]resorcinarene to prepare tetra-aza calix[4]resorcinarene, which was subsequently reduced to tetra-aminocalix[4]resorcinarene. The tetra-amino intermediate was then condensed with different aromatic aldehydes to prepare corresponding Schiff-base derivatives. Complexation behavior of these newly synthesized derivatives with Cu(II) in chloroform was also investigated by liquid-liquid extraction.

2. Results and Discussion

Though the resorcinarene chemistry is more than half a century old, the tetra-aminocalix[4]resorcinarene,

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which could be extremely useful and desirable precursor for functionalization of 'upper rim', has not been reported till date. The traditional way to introduce amino group in calixarene chemistry is nitration, followed by reduction of the nitro group with common reducing agents.[15,16] However, neither nitration of calix[4]resorcinarene nor nitro-calix[4]resorcinarene has been reported yet. Cram et al.[17] have unsuccessfully attempted cyclization of 2-nitroresorcinol to obtain tetra nitro calix[4]resorcinarene. During our attempts at nitration of calix[4]resorcinarene, we found that all the protocols normally used in 'classical' chemistry did not work in this case. The formation of nitro compound was never observed under the conditions tested (conc. HNO_3 or 100% HNO_3/CH_2Cl_2 or acetic acid, 100% HNO_3/CF_3COOH, $NaNO_3/CF_3COOH/AlCl_3$).

ting with concentrated hydrochloric acid). The ^1H NMR analysis of the tetra-azo intermediate **2** (obtained by reaction with diazonium salt of *para*-aminobenzoic acid) revealed two doublets due to the *para*-substituted phenyl rings at δ 7.76 and 7.89 ppm with typical coupling constant 8.2Hz(J), together with singlet at δ 9.87 (OH) and δ 1.65 (CH_3). The IR spectra exhibited C=O stretching at 1698 cm^{-1} and hydrogen bonded –OH stretching at 3167 cm^{-1}.

Having synthesized the tetra-azo intermediate, we attempted several different reduction procedures described in the literature to prepare tetra-amino intermediate.[15,19,20] Reduction of the azo compound **2** using $Na_2S_2O_4$ in boiling aq. NaOH solution was found to be the most efficient procedure to achieve tetra-amino intermediate.[20,21] The expected product tetra aminocalix[4]arene **3** was iso-
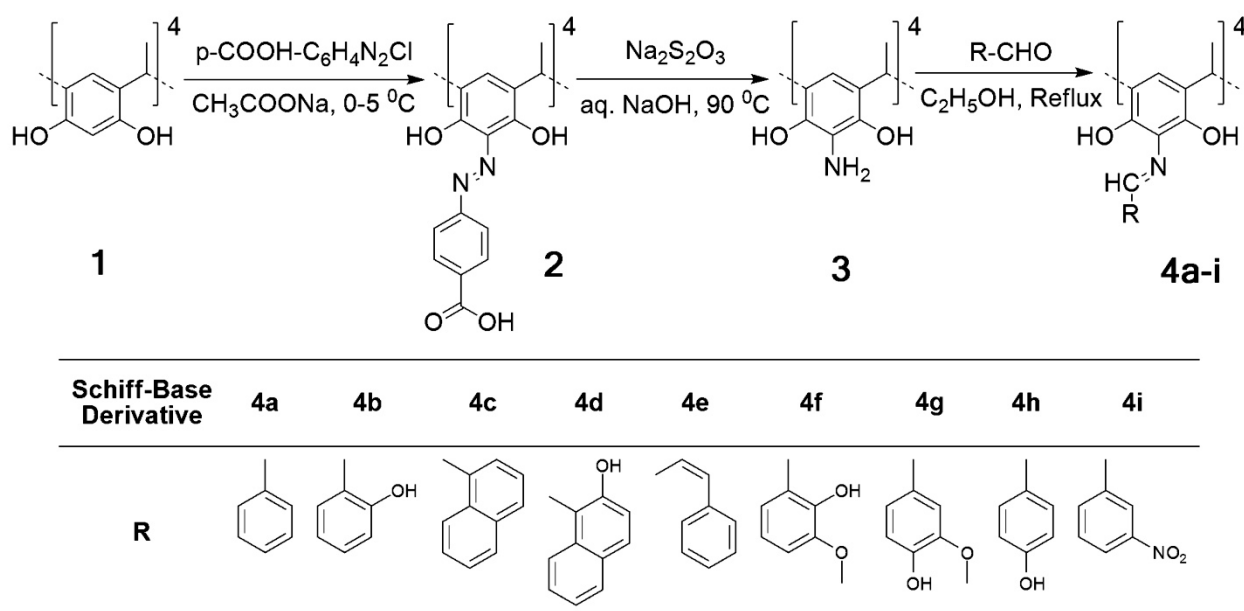
Scheme 1. Synthetic route for **4a-i**.

Thus, a new method was devised (Scheme 1) for the amination of the calix[4]resorcinarene **1** at the upper rim. The amination was achieved via tetra-azo intermediate **2**, which was prepared by diazotization of calix[4]resorcinarene with aromatic diazonium salts, a reaction well known in calixarene chemistry.[18] The reaction between calix[4]resorcinarene **1** and diazonium salt proceeded smoothly to yield the corresponding tetra-azo compound. The reaction was carried out using different diazonium salts of aniline, *para*-nitro aniline and *para*-amino benzoic acid, however, quantitative yields were obtained with the diazonium salt of *para*-amino benzoic acid in the presences of sodium acetate as base. The addition of the diazonium salt to a solution of **1** led to immediate color change (yellow to red), indicating the formation of azo compound. Stirring the reaction at room temperature gave colored precipitates that were purified by reprecipitation (dissolving in base and reprecipita-

lable as a pale yellow powder in 90% yield. The compound **3** was unstable in air and the original color quickly changed to black, however, it was moderately stable in the presence of 2N HCl as hydrochloride intermediate. The IR spectra revealed a broad peak at 3222 cm^{-1}, corresponding to –NH_2 and –OH stretching and 1231cm^{-1} for C–N, str. The ^1H NMR spectrum (300 MHz, DMSO-d_6) showed only a single peak at δ 7.2 ppm which was presumably due to aromatic protons of resorcinarene framework.

Condensation of the newly synthesized tetra-amino-calix[4]resorcinarene with different aromatic aldehydes (benzaldehyde, salicylaldehyde, naphthaldehyde, 2-hydroxy naphthaldehyde, cinnamaldehyde, o-vanillin, vanillin, *para*-hydroxy benzaldehyde and m-nitro benzaldehyde) in dry alcohol gave corresponding Schiff bases **4a-i** in moderate yields. The synthetic reaction sequence is depicted in Scheme 1.

Table 1: Spectroscopic data for **4a-i**

Derivative	λ_{max} (nm)	Molar absorptivity (l mol^{-1} cm^{-1})
4a	360	8.14×10^3
4b	380	1.42×10^4
4c	360	7.76×10^3
4d	370	1.01×10^4
4e	360	7.84×10^3
4f	360	9.92×10^3
4g	360	9.36×10^3
4h	360	8.70×10^3
4i	360	8.93×10^3

Extraction studies of synthesized Schiff-bases were carried out, to analyze their complexation behavior towards transition metal ions, in particular with Cu(II), by liquid-liquid extraction in chloroform-water two phase system. The organic layer was separated, dried over sodium sulfate and diluted uniformly. The extract was then analyzed by UV-Visible spectrometry to detect any complexation that might have occurred. The complexation was evident by a shift of nearly 80 nm as compared to λ_{max} of ligand (290 nm) in almost all the cases (Figure 1). Table 1 lists the spectral characteristics apparent from the ex-
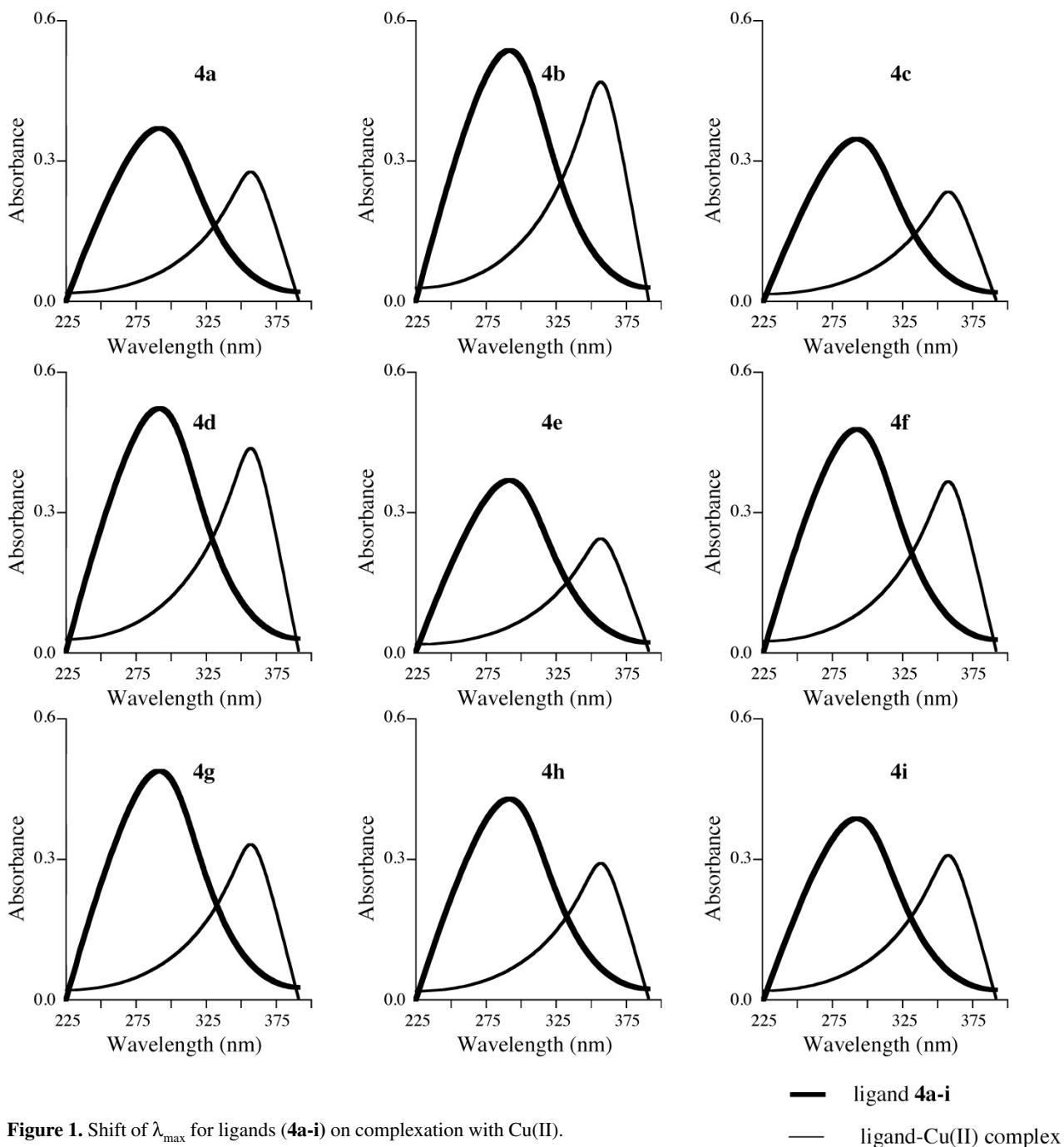
Figure 1. Shift of λ_{max} for ligands (**4a-i**) on complexation with Cu(II).

— ligand **4a-i**

— ligand-Cu(II) complex

traction studies with Cu(II). In addition to a prominent change in λ_{max}, the results also indicate high molar absorptivity, which may imply that these Schiff bases can prove to be very sensitive agents for detection/determination of Cu(II) ions.

3. Experimental

3. 1. General

Melting points were taken in a single capillary tube using a Toshinwal (India) melting point apparatus and were uncorrected. Elemental analysis was done on Heraeus CarloEbra 1108 elemental analyzer. IR spectra were recorded on a JASCO FTIR-410 ratio recording infrared spectrophotometer as KBr pellets and expressed in cm^{-1}. ^{1}H NMR spectra were recorded on Bruker DRX 300 NMR spectrometer operating at 300 MHz for proton in DMSO-d_6 with tetramethylsilane as internal standard. Mass spectra were recorded on JEOL SX 102 / DA 6000 mass spectrometer using xenon/argon (6 KV, 10mA) as the FAB-gas. The accelerating voltage was 10 KV and the spectra were recorded at room temperature. UV absorption studies were carried out on a JASCO 570 UV/VIS/ NIR spectrophotometer.

3. 2. Synthesis

3. 2. 1. Synthesis of Tetra-azo Product 2

Para-amino benzoic acid (1.37 g, 10 mmol) and 2 ml conc. HCl were added to 15 ml water and the resulting solution was cooled to 0 °C. To this mixture, a solution of NaNO$_2$ (0.8 g, 11.6 mmol) in 10 ml water was added drop wise with continuous stirring at such a rate to maintain the temperature below 5 °C. The resulting mixture was slowly added to a solution of calix[4]resorcinarene **1** (5 g, ca. 1 mmol) and sodium acetate (5 g) in 20 ml water at 0–5 °C. The reaction mixture was stirred for 15 min at the same temperature, allowed to stay at room temperature for 2 h and then heated to 60 °C for 30 min. The mixture was acidified with 2M HCl (10 ml). The resulting precipitates were collected by filtration and washed repeatedly with water and methanol. The solid obtained was dissolved in a saturated solution of NaHCO$_3$ and re-precipitated with conc. HCl. The mixture was stirred overnight at room temperature, filtered and washed with water and methanol successively, and dried overnight at 80 °C to give essentially pure **2** as a red-brown solid, yield 78%, mp >300 °C (dec).

3. 2. 2. Synthesis of Tetra-amino-calix[4] resorcinarene 3

The azo compound **2** (5 g, 0.5 mmol) was dissolved in NaOH solution (0.5 g in 25 mL water). To the resulting dark-red solution, Na$_2$S$_2$O$_4$ (2.5 g, 15 mmole, added as 250 mg portions after every 5 min) was added and heated for 1 h at 90 °C with constant stirring. The reaction mixture was cooled to room temperature and 40 ml conc. HCl was added. The resulting pale yellow precipitates were filtered instantly over a glass frit with the help of vacuum and washed rapidly with dil. HCl, followed by conc. HCl and methanol respectively. The product was dried at reduced pressure to give 1.2 g of **3**. The solid was stable for ca. 6 h at ambient temperature as hydrochloride salt. Before coupling with aldehyde, the amine was shaken briefly (30 sec) with saturated bicarbonate solution and filtered immediately over a glass frit under vacuum. The process was repeated with degassed distilled water and dry ethanol. Finally the tetra-amine was suspended in dry ethanol and coupled immediately with appropriate aldehyde.

3. 2. 3. General Synthesis of Calix[4] resorcinarene Schiff Bases (4a-i)

A mixture of **3** (1 gm, 1.655 mmol) and an appropriate aldehyde (8.275 mmol) were taken in 50 ml of dry ethanol, refluxed for 3 h in a 100mL round bottom flask and then allowed to cool down to ambient temperature spontaneously. After 1 hour, needle shaped light brown to yellow colored large crystals of product were observed. The reaction mixture was kept undisturbed overnight to allow maximum crystallization. The crystals were subsequently filtered, washed with warm alcohol-acetone mixture (1:1, v/v) and dried under vacuum to give **4a-i** in 54–64% yield. If the reaction is performed on larger scale (>5 g), some moisture removal system should be employed.

3. 3. Characterization Data

2: Yield 78%, mp >300 °C (dec), color: brown; IR (KBr): ν 3168cm^{-1} (–OH), 1698cm^{-1} (C=O); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.65 (d, 12H, CH$_3$), 4.63 (q, 4H, bridge CH), 9.49 (s, 8H, OH), 7.76–7.89 (d:d, 1:1, J=8.2 Hz, 16H, =NC$_6$H$_4$COO), 7.30 (s, 4H, ArH-calix); MS (m/z): 1138 (M+1); Elemental Anal. (%) calcd. for C$_{60}$H$_{48}$N$_8$O$_{16}$: C 63.38, H 4.25, N 9.85. Found: C 63.58, H 4.24, N 9.69.

3: Yield ca. 90% (depends upon rapidity of isolation procedure), color: pale yellow; IR (KBr): ν 3222cm^{-1} asymmetric (–NH$_2$ and –OH), 1231cm^{-1} (C–N); ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.20 (s, 4H, ArH); MS (m/z): 626 (M+2HCl); Determination of melting point and elemental analysis were not possible due to highly unstable nature of the compound.

4a: Yield 60%, mp 165 °C, color: yellow; IR (KBr): ν 3426cm^{-1} (–OH), 1634cm^{-1} (–N=CH); ^{1}H NMR (300 MHz, DMSO-$d6$): δ 1.65 (d, 12H, CH$_3$), 4.63 (q, 4H, bridge CH), 9.49 (s, 8H, OH), 8.82 (s, 4H, N=CH), 7.3–7.9 (d:t:t, 2:2:1, J=7.9 Hz, 20H, ArH); MS (m/z): 958 (M+1); Elemental Anal. (%) calcd. for C$_{60}$H$_{52}$N$_4$O$_8$: C 75.29, H 5.48, N 5.85. Found: C 75.38, H 5.44, N 5.60.

4b: Yield 62%, mp 180 °C, color: yellow; IR (KBr): ν 3403cm^{-1} (–OH), 1604cm^{-1} (–N=CH); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.65 (d, 12H CH$_3$), 4.63 (q, 4H, bridge CH), 9.50 (s, 12H, OH), 8.82 (s, 4H, N=CH) 7.2–7.9 (s:d:t, 1:2:1, J=7.2 Hz, 16H, ArH); MS (m/z): 1022 (M+1); Elemental Anal. (%) calcd. for C$_{60}$H$_{52}$N$_4$O$_{12}$: C 70.58, H 5.13, N 5.49. Found: C 70.49, H 5.10, N 5.55.

4c: Yield 64%, mp 170 °C, color: yellow; IR (KBr): ν 3346 cm^{-1} (–OH), 1614 cm^{-1} (–N=CH); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.64 (d, 12H, CH$_3$), 4.64 (q, 4H, bridge CH), 9.58 (s, 8H, OH), 8.88 (s, 4H, N=CH) 7.3–7.8 (d:t:d:t, 2:2:2:1, J=7.3 Hz, 32H, ArH); MS (m/z): 1158 (M+1); Elemental Anal. (%) calcd. for C$_{76}$H$_{60}$N$_4$O$_8$: C 78.81, H 5.22, N 4.48. Found: C 78.77, H 5.10, N 4.72.

4d: Yield 58%, mp 168 °C, color: brown; IR (KBr): ν 3473 cm^{-1} (–OH), 1610 cm^{-1} (–N=CH); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.64 (d, 12H, CH$_3$), 4.62 (q, 4H, bridge CH), 9.50 (s,12H, OH), 8.82 (s, 4H, N=CH) 7.3–7.9 (d:t:d:d, 2:2:1:1, J=7.5 Hz, 7.7, 28H, ArH); MS (m/z): 1222 (M+1); Elemental Anal. (%) calcd. for C$_{76}$H$_{60}$N$_4$O$_{12}$ C74.74, H 4.95, N4.59. Found: C 74.98, H 4.9 4, N 4.60.

4e: Yield 56%, mp 175 °C, color: creamish; IR (KBr): ν 3463 cm^{-1} (–OH), 1617 cm^{-1} (–N=CH), 931(CH=CH); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.65 (d, 12H, CH$_3$), 4.63 (q, 4H, bridge CH), 4.6 (d, 8H, CH=CH), 9.61 (s, 8H, OH), 8.89 (s, 4H, N=CH), 7.3–7.5 (d:t:t, 2:2:1, J=7.4 Hz, 24H, ArH); MS (m/z): 1062 (M+1); Elemental Anal. (%) calcd. for C$_{68}$H$_{60}$N$_4$O$_8$: C 76.96, H 5.70, N 5.27. Found: C 76.90, H 5.69, N 5.10.

4f: Yield 56%, mp 167 °C, color: light brown; IR (KBr): ν 3425 cm^{-1} (–OH), 1630 cm^{-1} (–N=CH); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.65 (d, 12H, CH$_3$), 2.72 (s, 12H, OCH$_3$), 4.63 (q, 4H, bridge CH), 9.60 (s, 12H, OH), 8.87 (s, 4H, N=CH) 7.3–7.5 (d:t:t, 1:1:1, J=7.7 Hz, 16H, ArH); MS (m/z): 1141 (M+1); Elemental Anal. (%) calcd. for C$_{64}$H$_{60}$N$_4$O$_{16}$: C 67.36, H 5.26, N 4.91. Found: C 67.42, H 5.50, N 4.92.

4g: Yield 54%, mp 155 °C, color: yellow; IR (KBr): ν 3415 cm^{-1} (–OH), 1622 cm^{-1} (–N=CH); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.65 (d, 12H, CH$_3$), 2.70 (s, 12H, OCH$_3$), 4.65 (q, 4H, bridge CH), 9.71 (s, 12H, OH), 8.82 (s, 4H, N=CH), 7.4–7.9 (s:d:d, 1:1:1, J=7.5 Hz, 16H, ArH); MS (m/z): 1141 (M+1); Elemental Anal. (%) calcd. for C$_{64}$H$_{60}$N$_4$O$_{16}$: C 67.36, H 5.26, N 4.91. Found: C 67.41, H 5.50, N 4.90.

4h: Yield 60%, mp 170 °C, color: yellow; IR (KBr): ν 3410 cm^{-1} (–OH), 1604 cm^{-1} (–N=CH); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.64 (d, 12H, CH$_3$), 4.64 (q, 4H, bridge CH), 9.68 (s, 12H, OH), 8.89 (s, 4H, N=CH), 7.3–7.4 (d:d, 1:1, J=7.6 Hz, 20H, ArH); MS (m/z): 1022 (M+1); Elemental Anal. (%) calcd. for C$_{60}$H$_{52}$N$_4$O$_{12}$: C 70.58, H 5.14, N 5.49. Found: C 70.39, H 5.19, N 5.45.

4i: Yield 60%, mp 162 °C, color: creamish; IR (KBr): ν 3222 cm^{-1} (–OH), 1606 cm^{-1} (–N=CH), 1508 (N–O); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.63 (d, 12H, CH$_3$) ,4.64 (q, 4H, bridge CH), 9.63 (s, 8H, OH), 8.89 (s, 4H, N=CH), 7.3–7.9 (s:d:t:d, 1:1:1:1, J=8.0 Hz, 20H, ArH); MS (m/z): 1138 (M+1); Elemental Anal. (%) calcd. for C$_{60}$H$_{48}$N$_8$O$_{16}$: C 63.77, H 4.25, N 9.85. Found: C 62.59, H 4.15, N 9.70.

3. 4. Extraction Studies

For complexation studies, stock solutions of ligands **4a-i** (1.0 × 10^{-2} M) were prepared by separately dissolving appropriate amounts of each in 1L of chloroform. The Cu(II) stock solution (4.0 × 10^{-2} M) was prepared by dissolving appropriate amount of CuSO$_4$ · 5H$_2$O in 1L of double distilled water. The stock solutions were diluted 100-folds to obtain working solutions of 1.0 × 10^{-4} M and 4.0 × 10^{-4} M for **4a-i** and Cu(II) respectively. For extraction studies, 10 ml of ligand solution, 5 ml metal solution and 5 ml aq. buffer (pH 4.7) were mixed and shaken for 30 min. The organic layer was separated through a separatory funnel, dried with Na$_2$SO$_4$ and diluted uniformly. Solutions thus prepared were examined for UV-Vis absorptions at suitable wavelengths.

4. Conclusion

A new approach was developed to synthesize the tetra-aminocalix[4]resorcinarene. This amino derivative can serve as a key intermediate for further functionalization to obtain calix[4]resorcinarene with specific receptor properties. Nine new calix[4]resorcinarene Schiff-bases were synthesized and characterized. Their complexation behaviour with Cu(II) was studied by liquid-liquid extraction. Further studies are underway to explore the complexation abilities of these new ligands with other transition metal ions.

5. References

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Abstract

V prispevku je podana sinteza nekaterih novih Schiffovih baz, ki so funkcionalizirane na zgornjem obroču kaliks[4]rezorcinarenov. Pripravljene so bile z reakcijo tetra-aminokaliks[4]rezorcinarenov z različnimi aromatskimi aldehidi pri refluksu etanola. Tetra-aminokaliks[4]rezorcinareni, ki lahko služijo kot zelo dobri prekurzorji za derivatizacije na posebnih obročnih mestih kaliksarenov, so bili prvič pripravljeni preko tetra-azo intermediata. Avtorji prispevka so prvo uvedli azo skupino na zgornji obroč in jo nato reducirali z Na_2S_2O4 v vodnem NaOH. Sintetizirane Schiffove baze so bile okarakterizirane z elementno analizo, FT-IR, NMR in masno spektroskopijo. Raziskana je bila tudi njihova sposobnost kompleksacije z Cu(II) ioni.